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Electrical Methods for Diamond-Die Production

By Chauncey G. Peters, Walter B. Emerson, Karl F. Nefflen, Forest K. Harris, and Irvin L. Cooter

Electrical methods to drill diamond have been developed and applied to the making of diamond wire-drawing dies 0.0005 to 0.0015 of an inch in diameter that heretofore were produced solely by mechanical operations. The time required to produce excellent dies is reduced materially by applying these electrical methods to the following operations: 1, Pilot drilling the primary cone with a high-voltage spark in air; 2, drilling the secondary cone with a low-voltage spark in an electrolyte.

These two methods of drilling are described and their application to the making of small dies at the National Bureau of Standards is given in detail.

I. Introduction

In recent years there has been a remarkable increase in the use of diamond for industrial purposes. About 10 percent of the available supply of industrial diamonds is now required to produce diamond dies for drawing fine wire of uniform diameter.

The following statement is quoted from an article by Paul L. Herz, "Diamonds in the wire-drawing industry": [1]

> Up to 50 years ago steel drawplates or ruby or sapphire dies were used for drawing fine wire, and it was necessary to draw the wire slowly. Because the die wore rapidly, increasing the size of the hole, it was difficult to produce accurately gaged wire. In later years dies of tungsten, molybdenum, or boron carbide have competed with diamond dies. Diamonds, however, enjoy an exclusive field for the harder and tougher wire materials, such as chrome-nickel resistance wire, brass and phosphor bronze wire, and high-carbon steel wire. Diamond is also used for drawing electrolytic copper wire from the smallest sizes up to diameters approaching 0.080 in. In addition, diamond is indispensable whenever precision of size and perfect roundness are essential considerations.

Previous to the cutting off of imports from Europe when France and the Low Countries were invaded in 1940, all small diamond dies were imported because labor costs made their manufacture in this country unprofitable. At the request of the War Production Board in January 1943, the National Bureau of Standards undertook an investigation to improve the manufacturing processes and the quality of diamond dies 0.002 to 0.0005 in. in diameter in order to meet the requirements for many vital war products. This work was carried on as a joint investigation by the Miscellaneous Minerals Division of the War Production Board and the National Bureau of Standards until July 1, 1943, when administration of the investigation was transferred to the War Metallurgy Committee of the National Research Council.

A diamond die laboratory was installed at the National Bureau of Standards with equipment for studying and testing existing die-drilling and wire-drawing machines and processes, and for developing new methods and new equipment to meet the designated aims of the investigation, namely: (a) to reduce production time and cost, (b) to improve the quality of domestic dies. By the introduction of electrical methods of drilling, both objectives were attained so successfully that users of small-size dies are no longer dependent on foreign importations.

The present paper, superseding the Bureau's final report, Investigation of Small Diamond Dies, NRC–535, Serial No. W–144, September 21, 1944, isued to the War Metallurgy Committee of the National Research Council, includes new developments made at the National Bureau of Standards after the termination on July 1, 1944,

[1] Paul L. Herz, Diamonds in the wire-drawing industry, Am. Mineral. 27, p. 171 to 175 (1942).

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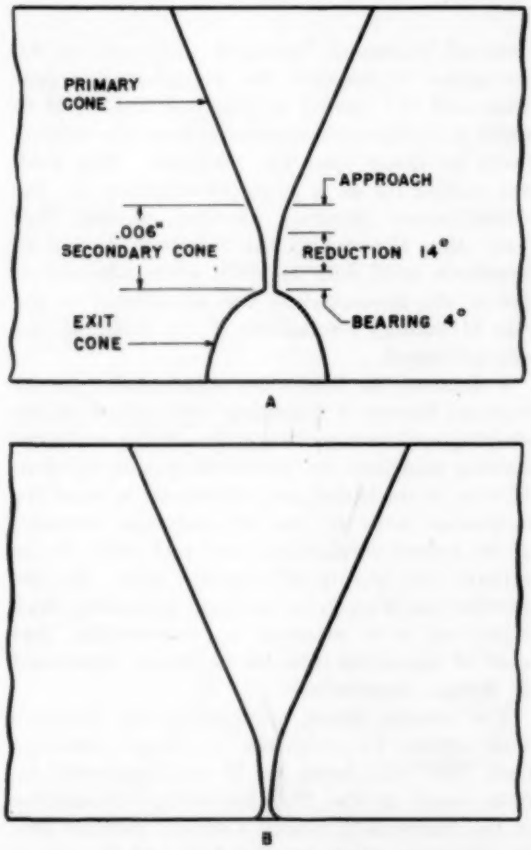
of the die investigation as a joint project with the War Production Board and the National Research Council.

II. Description of Small Diamond Dies

Diamonds weighing one-sixth to one-fourth carat, free from flaws and inclusions, and of symmetrical shape are selected for making small dies, i. e., dies of less than 0.002 in. in diameter. The top and bottom surfaces are made plane and parallel, and a side facet is cut perpendicular to these surfaces to serve as a window through which the profile of the die and the progress of drilling may be observed.

The shape of a wire die is governed by the work it is required to perform. Figure 1A, shows the customary profile, together with the necessary elements comprising a satisfactory die for drawing resistance alloy and steel wires. The shape of primary, approach, and exist cones are of secondary importance to the actual working parts of the die, i. e., the reduction and bearing cones, which should be properly shaped and highly polished. A slight rounding-off, or relief, of the bearing cone at its junction with the exit cone, when present, tends to reduce chipping of the diamond during the wire-drawing operation.



FIFURE 1.—*Profiles of dies.*
A, Exit-cone die; *B*, flat back die.

Examination of many used dies, however, indicated failure by chipping at the intersection of the bearing and exit cones. This was ascribed to strain and minute fractures in the diamond introduced by the mechanical operations used in forming the exit cone. Figure 1, B, shows the profile of dies produced at the National Bureau of Standards, in which the exit cone is eliminated by lengthening the primary cone and having the secondary cone pierce the relatively unstrained back surface produced by means of a rotating cast-iron lap, with fine diamond powder as an abrasive.

III. Mechanical Drilling of Dies

1. Mechanical Method

Methods and equipment developed in Europe for drilling diamond dies employ essentially a star drilling action. The drilling machine has a single horizontal spindle that rotates a sharpened steel sewing needle at high speed. The diamond is mounted in a holder that rests on rollers and is free to move back and forth parallel to the axis of the drilling needle. Drilling is accomplished by oscillating the diamond against the rapidly rotating needle. Diamond powder of different grades mixed with oil is used as the abrasive.

Domestic machines operate on the same principle as the European design but usually have 10 vertical spindles.

The following operations are required to drill a die by the mechanical method:

Spotting.—The blank is mounted and centered in a metal disk that is rotated in a bench lathe. A small hole is started in one of the flat surfaces of the stone with a diamond chip held in a pair of pliers. This operation is designated by makers of diamond tools as "bruting." The cavity thus formed serves as a starting hole for the drill.

Drilling the primary cone.—A steel needle about 0.040 in. in diameter and with a rather blunt

point is used to drill the primary cone. Relatively coarse diamond abrasive powder is used at the start to speed up the coning operation. Finer powder is substituted as the cone nears completion.

Drilling the secondary cone.—A lighter drilling machine with a fine needle ground to the approximate shape of the desired cone is used to produce the secondary cone. As the drilling proceeds, the needle must be recharged with the required size powder, reground as it wears, and reshaped to give the desired profile to the die. Drilling of the secondary cone is a tedious and time-consuming operation because of the necessarily small size of abrasive particles, needle diameters, and pressures on the needle that can be used.

Back opening.—After completing the fine drilling, the die is returned to the bench lathe for counter drilling. A spherical hole in line with the die axis is bruted into the back surface of the die with diamond chips held in sharp-nosed pliers until it reaches the secondary cone. In some shops bruting is discontinued when the sphere is within 0.003 in. of the cone. The final opening is then made on the drilling machine with a relatively blunt needle.

Polishing.—The polishing operation, performed on a polishing machine, is designed to smooth out any rings formed during the drilling, to smooth the ragged edges where the needle broke through from the back, and to give a fine polish to the working parts of the die.

2. Drilling Time

The following time data for these drilling operations for 0.0007- to 0.0010-in. dies were obtained from foreign reports and from experience gained in the Bureau's Interferometry Section with similar equipment:

	Time required		
	Holland	England	NBS
	hr	*hr*	*hr*
Primary cone	15	50	12 to 26
Secondary-cone drilling	75	120	80 to 100
Back opening	6	----	8
Polishing	15	----	20

Improved machinery and drilling technics enable American die makers to reduce appreciably the time formerly required to rough-drill the primary cone.

A more detailed description of the mechanical method of making dies, together with illustrations of the required machinery, is given by Grodzinski.[2]

IV. Introduction of Electrical Drilling to Die Making

A study of the operations involved in making dies by customary mechanical methods indicated that (1) improvement in the quality of a die could be expected from more painstaking attention to details of shape and finish, and (2) no great reduction in manufacturing time could be expected unless radical improvements or innovations could be evolved.

In 1899 Wehnelt [3] found that by applying voltage to a circuit containing two electrodes, one of which dipped slightly and the other more deeply below the surface of an electrolyte, sparking occurred at the point of the first electrode, causing rapid interruptions of the current. This circuit became known as the Wehnelt electrolytic interrupter. Dawihl and Fritsch,[4] using this electrolytic method to obtain high frequencies, produced hemispherical holes about 0.30 mm in diameter and 0.25 mm deep in the surface of diamonds, with sulfuric acid as the electroltye. Some of the early experiments with electrolytic drilling at the National Bureau of Standards, however, gave small-diameter holes 0.002 to 0.003 in. deep and having the general appearance of the secondary cone of a die. As a result of further extensive investigation, cones of 0.006 to 0.008 in. in depth, 0.0005 to 0.0015 in. in diameter, of smooth bore, and having the correct contour for secondary cones of dies, were produced at the bottom of mechanically drilled primary cones in from 40 to 80 minutes under controlled conditions, thereby eliminating the many hours of tedious drilling required to produce a similar cone mechanically. Furthermore, these electrically drilled cones in contrast to those produced mechanically give no evidence of added strain to the diamond when examined in polarized light.

[2] Paul Grodzinski, Diamond tools (The Vail-Ballou Press, Binghamton, N. Y., 1944).
[3] A. Wehnelt, Elektrotech. Z. **20,** 76 (1899).
[4] W. Dawihl and O. Fritsch, Zat. Ver. Deut. Ing. **85,** No. 11, 265 to 268 (March 15, 1941).

A nonelectrolytic high-voltage method of drilling discovered by one of the authors was applied to pilot-drilling the primary cone, thereby further reducing production time of a die and effecting a saving in the amount of diamond powder required. This nonelectrolytic operation for pilot-drilling the primary cone will be designated "high-voltage method" to differentiate it from the "electrolytic method", by which the small secondary cone of a die is drilled.

V. High-Voltage Drilling Method

1. Apparatus

Cones 0.012 to 0.020 in. deep and having the contour shown in figure 2 can be drilled in diamond-die blanks in 10 minutes with the equipment shown in figure 3. The application of high-voltage drilling to the production of diamond dies is given in a subsequent section that outlines the details of the Bureau method of making small dies. The equipment consists of the following parts: Adjustable-ratio transformer V, 110/(0–135) v, 2 amp. Transformer T, 12,000 v, 60-cycle sign lighting, 150 va. Ammeter A, alternating-current, 2-amp range. Capacitor C, 0.004 μf, 20,000 v. Quenched gap G, series of four to eight gaps. Electrode E, 0.020 in. in diameter—70 percent Pt, 30 percent Ir wire. Brass block B, to support the diamond. Helical spring S, 100 turns of No. 22 enameled copper wire wound on a 9.5-mm mandrel, with platinum supporting hooks to insure electrical contact. This coil will apply

FIGURE 2.—*Cone drilled with high voltage.*

a 0.5-g load to the diamond when the electrode support is lowered 3 mm after contacting the diamond. Holder H, a 5-in. length of Pt-Ir tubing of 0.020-in. inside diameter, 0.040-in. outside diameter, into which the electrode is slipped, and a cylindrical weight to extend the spring 20 to 30 mm. A short length of Pt-Ir wire inserted into the upper end of the tube is bent to form a supporting hook. Elevating unit L, for raising and lowering the electrode. Rotating unit R, for rotating the electrode.

Figure 4 gives the wiring diagram. Leads from a 110-v 60-cycle alternating-current outlet are connected to the primary terminals of adjustable-ratio transformer V. The secondary of V is

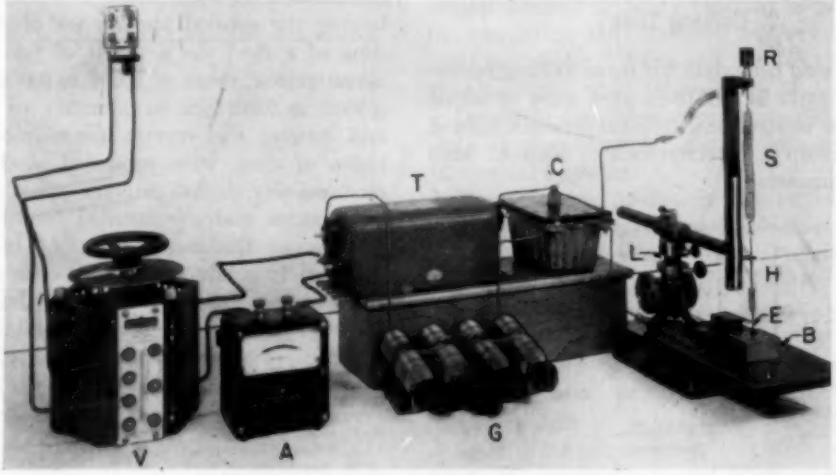


FIGURE 3.—*High-voltage drilling apparatus.*

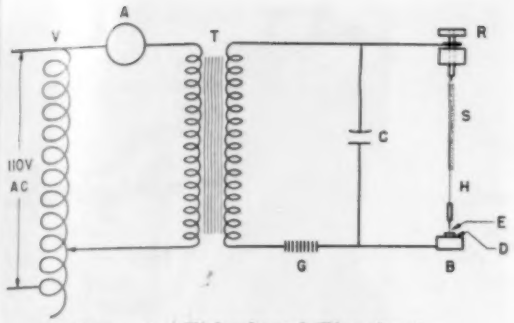


FIGURE 4.—*High-voltage drilling circuit.*

connected to transformer T. Ammeter A is connected between V and T to read the primary current of transformer T. One secondary terminal of T is connected electrically through the rotating device R, spring S, and holder H to the drilling electrode E; the other terminal is connected through gaps G to block B supporting diamond D; capacitor C, without which little or no drilling takes place, is connected between R and B. With the exception of V and A, the apparatus should be enclosed in a metal shield to reduce radio interference.

2. Drilling

Procedure.—The electrode, previously ground to a 20- to 30-degree tapering point, is lowered to contact the diamond resting on B, and its support is then lowered an additional 3 mm to give a 0.5 g load on the diamond. Voltage is applied to the circuit in increasing magnitude by means of the adjustable-ratio transformer. Sparking first occurs across the quenched gaps and, with increased potential, a discharge takes place across the surface of the diamond between the electrode and the metal block. Without the quenched gaps in the circuit, this discharge is a more or less continuous arc that tends to produce a dark deposit on the diamond that interferes with the drilling action. Further increase in voltage produces a more intense white spark. Drilling then proceeds at an accelerated rate. Satisfactory drilling takes place with this equipment with current values of 0.8 to 1.4 amp in the primary circuit. The best value depends upon factors not fully under control of the operator. Although drilling is most rapid with the higher power values, values large enough to cause the diamond to develop a frosted surface should never be used.

Rate.—Drilling is more rapid for the greater current values, as indicated by the following data:

Drilling time	Current	Cone depth
Min.	*Amp.*	*In.*
10	0.8	0.012
10	1.2	.016

The rate of drilling and also the quality of the cones is affected somewhat by the load on the diamond and the initial shape of the electrode. More rapid and better drillings were obtained with the selected load of 0.5 g than with loads of 0.2, 1.5, 3, or 8 g. Drillings with electrodes having a 20- to 30-degree taper and a tip diameter of 0.002 to 0.003 in. give excellent results. Deeper and better-shaped cones are usually obtained by drilling for 10-minute period and then redrilling with a resharpened electrode for another 10 minutes than by drilling with the same electrode for 20 minutes. An occasional rotation of the electrode during the drilling operation tends to produce better-shaped cones.

Although the drilling rate diminishes with increased cone depth and becomes very low when the depth exceeds 0.025 in., if a previously drilled cone is broadened by mechanical coning, electrical drilling will again proceed at a rapid rate.

Precautions.—Whenever a drilling is to be made in a flat surface of a diamond, sidewise motion of the electrode must be constrained. This is accomplished by passing the electrode through a hole of slightly greater diameter in a supported arm above the diamond, as shown in figure 3. Constraint is unnecessary when redrilling in a previously made cone. Movement of the diamond beneath the electrode is prevented by cementing it to its supporting surface with polystyrene lacquer or Duco cement.

The limiting condition for rapid drilling appears to be the power that can be applied before frosting of the diamond occurs. It has been found that frosting never results when the exposed electrode is operated below its reddening temperature, provided the diameter of the 70 percent Pt-30 percent Ir electrode is not greater than 0.020 in. With an electrode 0.032 in. in diameter, frosting occurred without visible reddening. Consequently, electrodes 0.020 in. in diameter should be used, and the current should be adjusted to

prevent visible reddening of the electrode immediately above the diamond. Although this is not a particularly fortunate criterion, its employment does permit rapid drilling without frosting of the diamond. It is evident, therefore, that high-voltage drilling at the present time is a process that requires continuous supervision by the operator. The spark should be viewed through protective glasses to avoid injury to the operator's eyes.

One other condition should be considered. As the drilling nears the bottom of the diamond, the current tends to be conducted through the diamond, the discharge around the diamond ceases, and the diamond tends to overheat. This condition may be overcome by mounting the diamond to be drilled upon another flat-surfaced diamond, silver-soldered in a cavity in brass block *B*, figure 3, and protruding about 0.5 mm above the metal surface, thereby insulating the die blank from the brass block.

VI. Electrolytic Method for Drilling Secondary Cones

1. Apparatus

The electrolytic method for drilling the secondary cones of small dies is a straightforward procedure requiring but a small amount of inexpensive equipment. It consists of the following parts: Variable-ratio transformer *V*, 110/(0–135) v, 2 amp. Ammeter *A*, alternating current, 0- to 1- or 0- to 2-amp range. Capacitor (optional) 10 μf, 600 v. Electrodes E_1 and E_2, hard-drawn 70 percent Pt-30 percent Ir wire, 0.020 in. in diameter. Elevating unit *L*, for raising and lowering E_1. Rotating unit *R*, for rotating E_1. Helical spring *S*, 75 turns of No. 30 enameled copper wire wound under slight tension on a 7-mm mandrel. Platinum suspension hooks are soldered to the ends of the coil to insure electrical contact. This coil will apply a load of about 0.1 g to the diamond when the electrode support is lowered 1 mm after the electrode contacts the diamond, and about 0.2 g when it is lowered 3 mm. The load may be increased by using larger wire or by decreasing either the diameter or the number of turns of the coil. Holder *H*, a 5-in. length of Pt-Ir tubing of 0.020 in. inside diameter, 0.040 in. outside diameter, into which E_1 is slipped, and a cylindrical weight to extend the spring *S*, 20 to 30 mm. A short length of Pt or Pt-Ir wire inserted in the upper end of the tube is bent to form a supporting hook. Electrode E_2 should be so mounted as to permit vertical adjustment. Glass container *G*, petri dishes 6 in. (150 mm) in diameter by 1 in. (25 mm) deep are satisfactory. A small glass pillar about 8 mm high is cemented in the bottom of the container to support the diamond. The assembled equipment is shown in figure 5. The wiring diagram is shown in figure 6.

FIGURE 5.—*Electrolytic drilling apparatus.*

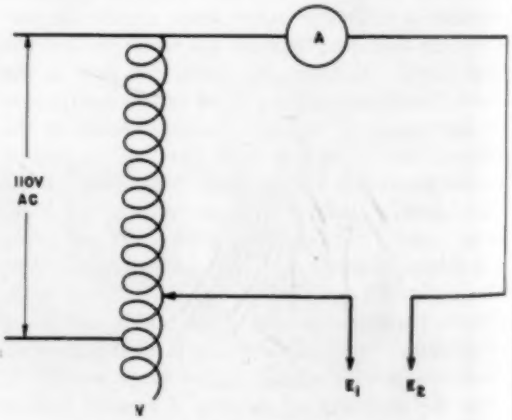


FIGURE 6.—*Electrolytic drilling circuit.*

2. Drilling Procedure

Electrode E_1 is centered in the previously formed primary cone of the die blank, which is cemented with polystyrene lacquer or Duco cement on the small glass pillar in the container. After the electrode touches the bottom of the cone, its support is lowered 3 mm to apply a predetermined load on the diamond. Electrode E_2 should dip 4 to 5 mm deeper than E_1. Electrolyte is then poured into the container until the diamond is immersed to a depth to give 0.5 to 0.7 amp when the correct drilling potential is applied.

By using a 10 percent, by weight, aqueous solution of KNO_3 as the electrolyte and applying 85 v across the electrodes, a small conical hole will be produced in the diamond. The shape of the cone is improved by occasionally rotating the drilling electrode. This rotation is accomplished by turning R through about 90 degrees. If, at the start, the drilling electrode E_1 had a 10-degree taper and a tip diameter of 0.001 in. the cone produced in 40 minutes will be 0.006 in. deep and have approximate top and bottom diameters of 0.002 and 0.0004 in., respectively. The tapered electrode will have shortened about 2 mm during the drilling operation, and its tip (A, fig. 7, A) will have the shape of the hole and be of somewhat smaller dimensions. If a more blunt electrode is used, the resulting cone will have the same general shape as in the first case, but will be less deep; the shortening of the electrode will be less, and its final profile will show a broad shoulder above its tip (A, fig. 7, B). This seems to indicate that drilling is retarded by the time required for the electrolytic etching of the electrode.

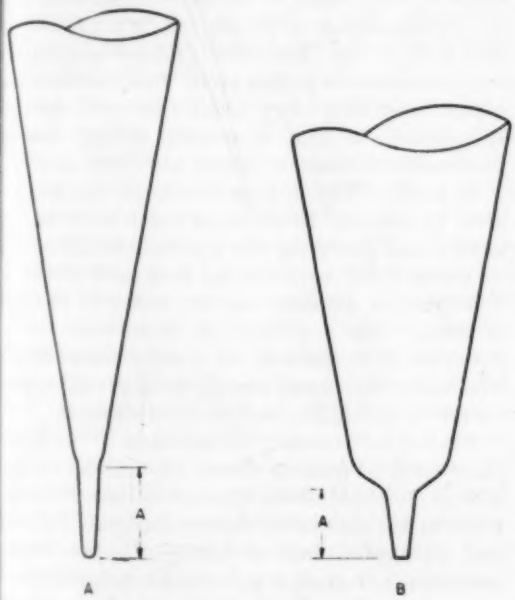


FIGURE 7.—*Drilling electrodes.*
A, With narrow shoulder; *B*, with broad shoulder.

3. Factors That Affect Drilling

Variables that affect the drilling are well within control of the operator, thereby permitting surprisingly close duplication of results. A discussion of several factors that affect the drilling follows.

ELECTRODES: *Composition.*—Both electrodes should be of a noble metal or an alloy of noble metals to withstand the electrolytic action. The composition of the deep-dipping electrode is less critical than that of the drilling electrode. The most satisfactory material tried thus far for the latter is hard drawn 70 percent Pt-30 percent Ir wire. Hard-drawn Pt wire drills fully as rapidly as this alloy but gives cones of somewhat greater diameter.

Diameter.—Electrodes 0.020 in. in diameter are sufficiently rigid to retain their shape during the pointing operation and are more economical to use than those of greater diameter.

Shape.—The drilling electrode is ground with an 8- to 10-degree taper to form a tip 0.001 to 0.002 in. in diameter. The rate of drilling is retarded if the tip diameter is large. The bottoms of the cones tend to be somewhat irregular when tips less than 0.001 in. in diameter are used.

No attention need be given to the shape of the nondrilling electrode.

ELECTROLYTE: *Composition.*—From tests of aqueous solutions of 40 electrolytes, including salts, bases, acids, and several combinations of salts, potassium nitrate (KNO_3) was selected as the most desirable for drilling the secondary cone of the die. Although drilling is possible with many of the other electrolytes, these were discarded for various reasons, including slowness of drilling, inability to drill deep cones, roughness or irregularity of the cones, release of irritating fumes, critical requirements for duplication of drillings, and contour of the resulting cone. The majority

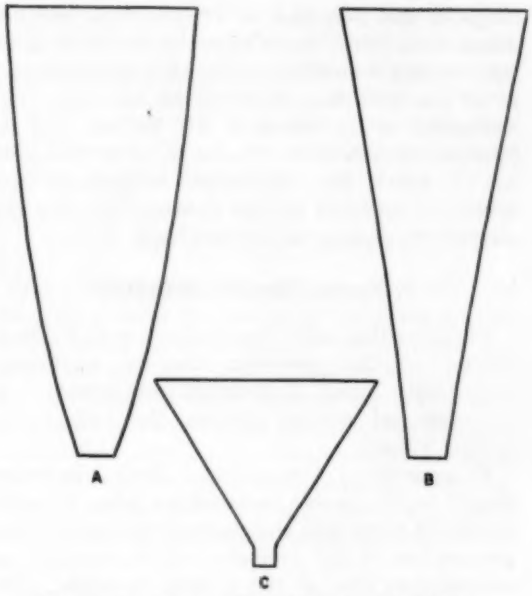


FIGURE 8.—*Cone profiles with various electrolytes.*
A, With several different electrolytes; *B*, with KNO_3; *C*, with NaCl.

of electrolytes give cones of contour *A*, (fig. 8) in contrast to the more desirable shape *B*, (fig. 8) for die secondary cones produced with KNO_3. One electrolyte, NaCl, gives a funnel-shaped cone *C*, (fig. 8) that has a useful application, to be discussed later, in making electrically drilled dies. Slight impurities in the electrolyte do not affect the drillings appreciably, but it is well to use distilled water. The addition of a small quantity (say, 0.2%) of aerosol to the solution reduces the spray from the liquid without interfering with the drilling.

Concentration.—Excellent drillings may be made with 3 to 10 percent KNO_3 concentrations and with 3 to 6 percent NaCl concentrations when the proper corresponding voltages and currents are used. Lower concentrations are less desirable from the standpoint of quality of the cones produced, whereas concentrations above the upper limits do not appear superior.

APPLIED LOAD.—In general, the magnitude of the load applied by the electrode to the diamond affects the diameter and depth of the cone. A load of 0.1 to 0.2 g is used to drill dies less than 0.001 in. in diameter. Dies of somewhat larger diameter are produced by increasing the weight. Drilling is not as rapid with the larger loads, however, and to drill a cone of the required depth with a 2-g load may necessitate resharpening the electrode and redrilling for an additional 40-minute period. The contour of the lower part of the cone tends to be irregular when loads of less than 0.1 g are used.

DRILLING PERIOD.—The rate of drilling obeys the law of diminishing returns. Cones 0.006 in. deep are produced in the first 40 to 45 minutes, after which the drilling proceeds rather slowly. With longer periods the bottoms of the cones tend to become slightly irregular in shape. The best procedure when deeper cones are required is to remove and resharpen the electrode after a 40-minute drilling. A second 40-minute drilling will then increase the cone depth to 0.0075 to 0.008 in. Cones of greater depth will require additional drillings.

EFFECT OF CAPACITANCE.—The effects upon drilling resulting from changes in the electrical characteristics of the circuit have been studied. Except for those effects produced by adding capacitance to the circuit, the results will not be reported at this time.

In parallel.—Two beneficial effects are noted when a capacitor of 5- to 10-μf capacitance is placed in parallel with the electrodes: (a) the shape of the bottom of the cone is improved, and (b) decomposition of the electrolyte is reduced, so that little, if any, attention is needed to maintain the solution at its proper level. One disadvantage noted in drilling very small dies with parallel capacitance is that a second drilling usually increases the diameter 0.0001 to 0.0003 in.

In series.—The drilling rate is greatly accelerated by placing 20-μf series capacitance in the circuit and increasing the potential to 220 to 230 v; cones 0.006 to 0.008 in. deep and 0.0012 to 0.0015 in. in diameter can be drilled in 15 to 20 minutes. The tendency of these cones to be irregular in shape and to wander from the die axis makes the use of this circuit inadvisable until better control of the cones can be attained.

VOLTAGE-CURRENT: *Relationship for different electrolytes.*—Figure 9 shows the voltage-current curves for three electrolytes of indicated concentrations for maximum current values of 0.8 amp and an applied load of 0.12 g. As the voltage increases from zero, a value *A* is reached for each electrolyte at which visible sparking begins. Sparking becomes more vigorous with increasing

voltage, until at voltage B the current suddenly becomes much lower. This transformation, unmistakable with NH_4Cl and H_2SO_4, is less obvious with KNO_3, although it may be readily determined by means of an oscilloscope. With NH_4Cl and H_2SO_4, the vigorous sparking subsides with the drop in the current and resumes when the current begins to increase again at C. The decrease in sparking is less evident with KNO_3, possibly because the current increases immediately after the transformation at B. These characteristics are common to many electrolytes.

Drilling of the diamond appears to begin at A and increases in rate until B is reached. Between B and C, the drilling electrode becomes highly polished, and little, if any, drilling takes place. Beyond C the electrode becomes pitted and rapidly deteriorates.

Drilling current.—For a given voltage, the current increases with the depth of immersion of the drilling electrode and the concentration of the electrolyte. With concentrations ordinarily used, shallow immersions giving currents less than 0.3 amp at transition B are unsatisfactory because the drilling action becomes irregular. Also, deep immersions giving currents greater than 1 amp are unsatisfactory because the drilling electrode becomes pitted. Immersions giving currents of 0.5 to 0.7 amp have proved the most satisfactory.

Drilling voltage. Drilling is most rapid for voltage values in the region of B *immediately before* transformation occurs. The voltage for best drilling increases as the concentration of the electrolyte is reduced and increases to a lesser degree with decrease in the applied load and with increase in the depth of immersion of the electrode. With electrolyte KNO_3, 0.2-g applied load, and 0.5- to 0.7-amp current, excellent cones are produced by using 85 to 90 v for 10-percent concentrations; 95 to 100 v for 5-percent concentrations, and 110 v for 4-percent concentrations. Excellent funnel-shaped holes are produced with electolyte NaCl by using 90 to 95 v and 110 v respectively, with 5-percent and 4-percent solutions. By selecting the proper concentration for a given electrolyte, maximum drilling will take place at line voltage, thereby eliminating the need for a variable-ratio transformer. Such a transformer, however, permits greater flexibility in drilling conditions.

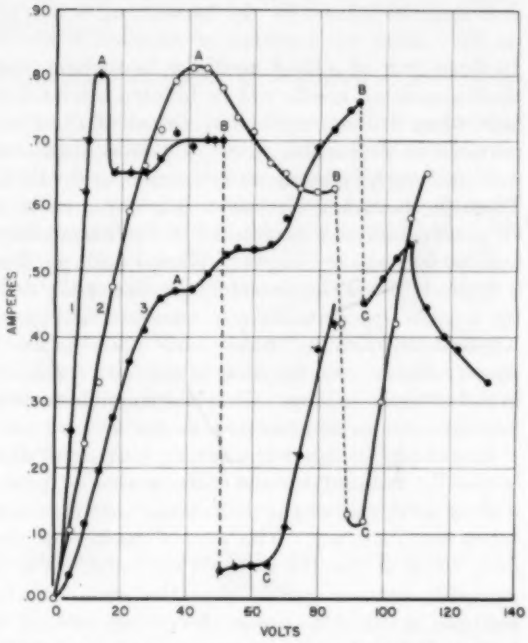


FIGURE 9.—*Voltage-current curves for* H_2SO_4, NH_4Cl, *and* KNO_3

Curve 1, 29% H_2SO_4+75% H_2O (by weight); 2, 8% NH_4Cl+92% H_2O (by weight); 3, 10% KNO_3+90% H_2O (by weight).

VII. Coning and Polishing Machine

As stated in section IV, electrical methods are used to pilot-drill the primary cone and to drill the secondary cone when making small dies at the Bureau. Mechanical operations are used to complete the primary cone and to polish the dies. These mechanical operations are performed much more effectively with a machine developed at the Bureau than with customary drilling and polishing machines.

Previous coning, or drilling, machines were designed to drill without the aid of pilot holes by tapping the diamond against a rapidly rotating steel needle, with diamond powder as the abrasive. This is essentially a combined grinding and star-drilling process in which grinding or drilling is caused by the action of the abrasive between the needle and the diamond. Deepening of the hole depends upon the breaking away of minute cleavage fragments by particles of diamond powder beneath the needle. Regardless of the speed of rotation, the axis of the drill is essentially stationary. Therefore, any forward progress of the

drill must be caused by the hammering action of its tip. Since the hardness of diamond is about 10 times that of a steel needle, it is obvious that the fine-pointed needle will be blunted after a few taps when drilling small dies. Most of the time required to drill a die of say 0.0006-in. diameter will consequently be spent in sharpening the drill. From the foregoing discussion it is apparent why 75 to 150 hours may be required to drill a secondary cone 0.006-in. in length. When drilling dies 0.003 to 0.080 in. in diameter, the size of the drill tip is sufficient to withstand considerable shock. Appreciable striking force and coarse-grained powder can be used for these larger dies, resulting in rather rapid drilling. This treatment, however, produces strains and fractures in the cone surface.

Regrinding of the drill when making small dies is greatly reduced by the introduction of pilot-drilling as the tip of the drill in this case does not touch the diamond. The conical surface of the drill, which is charged with abrasive and has considerable surface speed, cuts the cone to the required form—the action becoming less of a hammering and more of a grinding and cutting process. The multiple-head vertical-spindle machine, figure 10, for coning and polishing was designed to enhance this action by reducing the hammering action, giving a better flow of abrasive around the drill and affording a longer time of contact of the drill and diamond.

Each spindle of the machine (shown in fig. 11) runs in two cylindrical phosphor-bronze bushings, *B*, which are pressed into recesses in the crossbars and can be easily replaced when worn. The steel drilling needle, *N*, centered in a hole drilled in the axis of the spindle, *S*, is ground to the desired taper with a small hand grinder fitted with an Alundum wheel.

The oscillating rod, *R*, that supports the die also slides in two cylindrical bronze bushings. A U-shaped bronze spring, *U*, is attached to the lower end of each rod, and a cylindrical cap, *C*, having a hole of about 1-mm diameter drilled in its center fits onto the top of the rod.

Bar *D*, having an adjusting screw, *A*, in the outer end is attached at *F* to the rear crossbar by a flexure plate. This bar is moved up and down by the cam action of a shaft, *E*, having the end bearings turned eccentric to its axis. The speed of the shaft is governed by a 10-to-1 or 100-to-1 reduction gear box inserted between the counter and cam shafts.

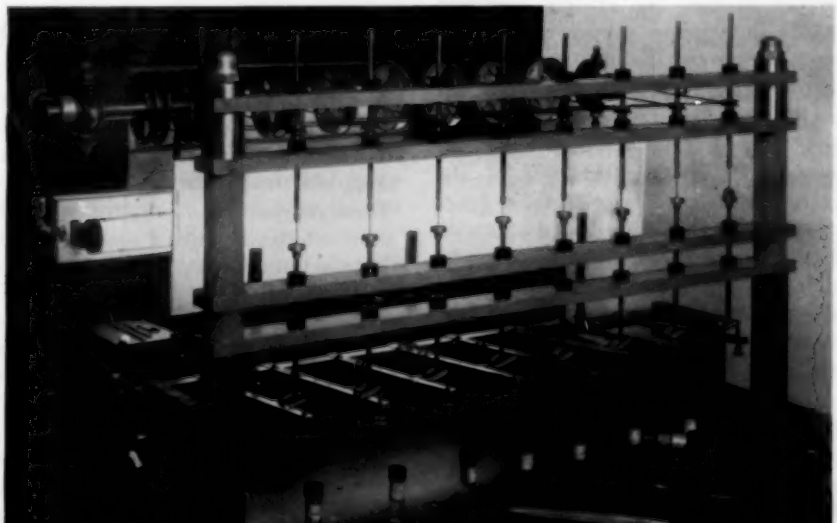


FIGURE 10.—*Machine for coning and polishing.*

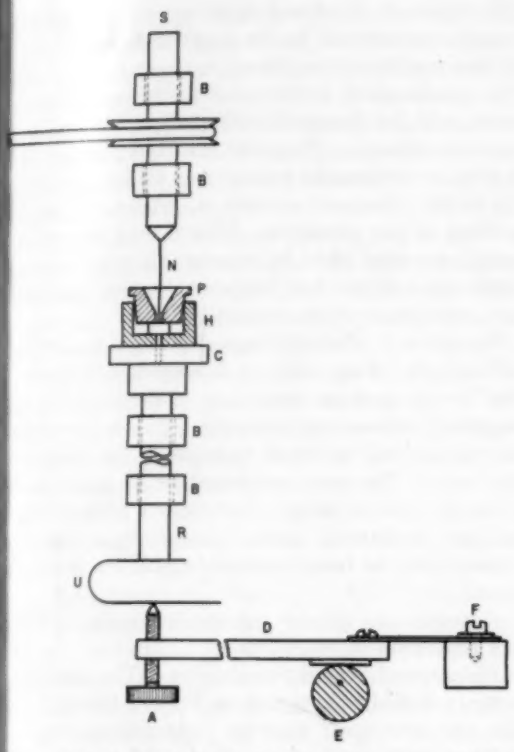


FIGURE 11.—*Individual spindle of coning and polishing machines*

The pressure exerted by the diamond on the needle and the time of contact of the two is regulated by adjusting the screw, *A*, and sliding it from the tip to the base of the bottom leaf of spring, *U*, by a rotation of the cam follower, *D*, about its point of attachment, *F*, to the rear crossbar.

For shaping or countersinking the primary cone, the die is held in a cylindrical cup, *H*, of about ½-in. external and ⅜-in. internal diameter. A plug, *P*, that fits the cup has a conical cavity drilled through from the top, which acts as a reservoir for the abrasive liquid. The top of the die is waxed to the bottom of the plug, which is then pressed firmly into the cup. The assembly is then placed on the cap, *C*, of the oscillator rod, where it slides sideways until the axis of the primary cone alines itself with axis of the drill. It is there coned until the tip of the drill reaches the bottom of the pilot drilling. The plug is easily removed with a pair of pliers, and the unmounted die can be examined for defects under good illumination with a microscope having a magnification of about 100 diameters.

VIII. NBS Method of Making Small Dies

The results obtained by the two electrical drilling methods may be summarized as follows: (1) High-voltage drilling—rough cones 0.012 to 0.020 in. deep and 0.003 to 0.004 in. in diameter can be drilled in 10 minutes. (2) Electrolytic drilling—smooth cones of correct size and contour for the secondary cones of small dies can be drilled in 40 to 80 minutes.

Considerable variation exists in the equipment and requirements of different die manufacturers. Consequently, each producer must determine how and to what extent he can apply these electrical methods most advantageously. The following step-by-step procedure is employed at the National Bureau of Standards to produce small dies.

1. Selection, Preparation, and Inspection of Die Blanks

Dies having a diameter of 0.002 in. or less require a thickness of 0.044 to 0.064 in. Diamonds of one-sixth to one-fourth carat suffice for this purpose.

The plane-parallel surfaces and the viewing window are cut on a rotating cast-iron lap, with diamond powder as the abrasive. The cutting action is accelerated at the Bureau by the application of an electric arc.[5]

After the three facets are cut, the diamonds are examined under the microscope. Those showing flaws, carbon spots, or other other imperfections in the central portion of the stone that might weaken the die or interfere with the drilling are rejected.

2. Drilling the Die

The sequence of operations used at the Bureau to produce small dies is given in figure 12, operations 1 to 10.

DRILLING THE PRIMARY CONE.—The primary cone is produced by a combination of high-voltage pilot drilling and mechanical coning, as indicated in figure 12, operations (1) to (6).

Operation 1. Spotting.—The blank is first cemented for high-voltage drilling on the pillar of brass block *B*, figure 3. The 0.020 in. 70 per-

[5] Chauncey G. Peters, Karl F. Neffien, and Forest K. Harris, Diamond cutting accelerated by an electric arc, J. Research NBS **34**, 567 (1945) RP1657.

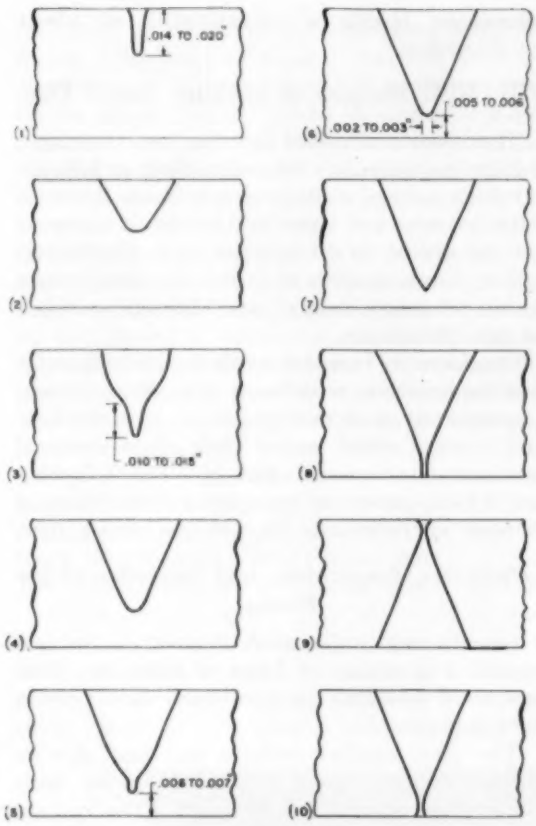


FIGURE 12.—*Sequence of drilling operations.*

Operations 1 to 6, drilling the primary cone; operations 7 and 8, drilling the secondary cone; operation 9, relieving the back opening; operation 10, polishing

cent Pt-30 percent Ir. electrode is ground with a 20-degree taper to form a 0.002 to 0.003 in. tip, and is constrained from sidewise motion by passing it through the hole in the supporting arm, and is centered on the upper surface of the blank. The elevating unit is next lowered 3 mm to give the required electrode pressure. Voltage is then applied to give an ammeter reading of 0.8 to 1.4 amp.[6] By continuing the drilling for 10 minutes a cone 0.014 to 0.020 in. deep, figure 12 (1) and figure 2, is produced that serves as a pilot hole for the next operation.

[6] These values represent the primary current in the high-voltage transformer, and will of course vary as different transformers are used. The operator will observe the intense blue-white spark between electrodes and across the face of the diamond, and may adjust the power by varying the input voltage until the needle electrode begins to show incandescence. The input voltage is then reduced to the point at which the electrode shows no redness, and the primary current is noted. Thereafter, the primary current in the transformer is a useful criterion of proper spark conditions.

Operation 2. First mechanical coning.— The cone is next countersunk to the shape in figure 12 (2), by means of the coning machine shown in figure 10. The spindle speed is about 5,000 rpm for this operation, and the diamond makes about 300 oscillations per minute. The drill is a steel needle 0.03 to 0.04 in. in diameter ground to a 45-degree point. Grade 40 [7] diamond powder in gelatin solution [8] is used as the abrasive. This coning operation usually requires 30 to 40 minutes; the actual man-hours required are few, however, because one person can operate 10 or more spindles.

Operation 3. Fore-drilling.—This is a repetition of the high-voltage drilling in operation 1, except that in this case no constraint of the electrode is required. Occasional rotation of the electrode during the drilling tends to improve the shape of the cone. The cone produced in 10 minutes is 0.010 to 0.015 in. deep. Serving as a pilot drilling for the mechanical coning operation, it reduces appreciably the time required to drill the primary cone.

Operation 4. Second mechanical coning.—This is a repetition of operation 2.

Operation 5. Final fore-drilling.—The diamond is again drilled as in operation 3. For this drilling the operator must exercise judgment as to the drilling time required to obtain the correct end point. The bottom of the drilled cone should be 0.006 to 0.008 in. from the back surface of the diamond. For exceptionally thick blanks, additional drillings and conings may be required.

Operation 6. Final coning.—Greater care is taken in this operation than in operations 2 and 4. The final primary cone, figure 12 (6), should be of symmetrical shape, free from drilling rings, and have either a polished or fine-matt surface. The diameter of the cone immediately above its apex should be between 0.002 and 0.003 in. to assure good blending of primary and secondary cones. Grade 20 diamond powder is used for the final coning operation.

DRILLING THE SECONDARY CONE: *Operation 7. Electrolytic drilling with* NaCl.—As noted in section VI, electrolyte NaCl gives a wide angle, funnel-shaped cone, whereas electrolyte KNO_3 produces a relatively long, narrow cone of correct

[7] See, NBS Commercial Standard CS 132-45, Grading of diamond powder (1945).

[8] Distilled water, 1 liter; gelatin, 1 g; sodium carbonate, 0.1 g (approximately) to give a pH of 9. Phenol crystals are added to prevent bacterial growth.

size and shape for the secondary cone of a small die. There is a tendency, however, for the secondary cone to be slightly to one side of the primary cone axis when a drilling with KNO_3 is made directly in a primary cone that has a broad, unpointed or irregular bottom. Excellent alinement and better blending of the primary and secondary cones are obtained by making a first drilling with NaCl as an electrolyte and a final drilling with KNO_3. In view of these advantages, the additional 30 minutes required for an NaCl drilling appears well spent. The following drilling procedure is used (see fig. 5 and section VI).

The 0.020 in. diameter 70 percent Pt-30 percent Ir drilling electrode is ground with an 8- to 10-degree taper to a 0.002 to 0.003 in. diameter tip. The diamond, previously cemented on the post in the container, is placed beneath and in the axis of the electrode. The electrode support is lowered an additional 3 mm after the electrode contacts the bottom of the primary cone to give about 0.2-g pressure on the diamond. The nondrilling electrode should dip about 4 to 5 mm deeper in the container than the drilling electrode. A 5-percent aqueous solution of NaCl is then poured into the container, immersing the diamond sufficiently (approximately 2 mm) to give a current of about 0.7 amp when 90 v are applied to the circuit. Drilling with 90-v potential is continued for 30 minutes. This gives a sharp apex to the cone, as shown in figure 12 (7).

Operation 8. Electrolytic drilling with KNO_3.—The procedure for drilling the secondary cone of the die is similar to that given for operation 7. However, for this drilling the electrolyte is a 10-percent aqueous solution of KNO_3, and the tip diameter of the drilling electrode is somewhat smaller, 0.0010 to 0.0015 in., for more rapid drilling. Current and voltage values are 0.7 amp and 90 v, respectively. Greater voltages will be required for rapid drilling if lower electrolytic concentrations are used. At the end of a 40- to 45-minute drilling period, the drill will have pierced the back face of the die, giving a smooth-bore cone having a length of about 0.006 in. and a diameter at the bottom of 0.0005 to 0.0006 in. Its general appearance is shown in figure 12 (8) and in figure 13.

If the initial distance between the bottom of the final primary cone and the back of the die

FIGURE 13.—*Die after piercing.* ×150.

was greater than 0.005 in., the drilling may not have pierced the back surface and an additional drilling with a resharpened electrode and a fresh solution of KNO_3 will be required.

RELIEVING THE BACK OPENING: *Operation 9. Giving the die back-relief.*—The sharp edge formed at the intersection of the secondary cone and the back surface is given a slight countersink to prevent damage by chipping when wire is drawn through the die. This is accomplished by inverting the die beneath the drilling electrode and drilling electrolytically from the back, using a 5-percent NaCl electrolyte. The electrode is ground with a 30-degree taper to a fine tip for insertion in the bottom of the secondary cone. Sufficient back-relief is obtained with a 4- or 5-minute drilling at 70 v and 0.5 to 0.7 amp, as shown in figure 12 (9 and 10). The appearance of the relief is somewhat improved by placing a 10-μf capacitance in parallel with the electrodes.

POLISHING: *Operation 10. Finishing the die mechanically.*—This operation is designed to improve the roundness of the die and to shape and polish its working parts.

The die is placed directly on the cap of the oscillator rod of the polishing machine, figure 11, which operates with a spindle speed of 7,000 rpm and oscillates the die 30 times per minute. A No. 7 to No. 10 steel sewing needle is ground to a long taper and, as it wears, is allowed to feed through the die into the hole drilled in the cap. The abrasive for polishing is diamond powder in pine

oil; grade 6 powder is used for fast cutting and grade 4 powder to produce the final polish.

The polishing operation is continued until the cone is circular, well-polished, and has a bearing of 0.001-in. length and 4-degree taper. The diameter of dies produced under the conditions described in operations 1 to 10 will usually be in the range of 0.0006 to 0.0008 in. Figure 14 shows two finished dies of 0.0008-in. diameter. Dies having short secondary cones have been drilled with diameters as small as 0.0003 in. Dies of 0.0010 to 0.0012-in. diameter are produced by increasing the load on the electrode or by using pure Pt electrodes when drilling the secondary cone. It has also been found that repeated drillings with 10-μf capacitance in parallel with the electrodes give larger diameter cones. For diameters greater than 0.0012-in., resort is made to mechanical enlargement on the polishing machine.

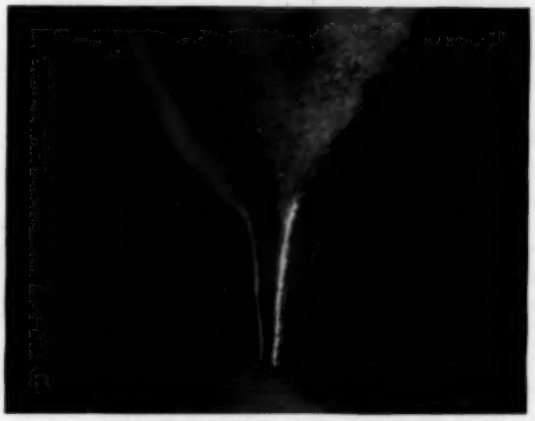


FIGURE 14.—*Finished dies.* ×150.
A, Flat-back type; *B*, exit-cone type.

CLEANING.—When dies become filled with foreign matter the usual procedure is to clean them with a pointed piece of wood or with a fine bristle brush and a solvent such as alcohol or gasoline. These methods work well with large dies but often fail with small dies because the secondary cone and bearing are much smaller than the bristles of the brush.

In the Bureau's laboratory the dies are cleaned with the high-voltage spark produced by the apparatus shown in figure 3. It is essential that the capacitor be removed from the circuit, figure 4, for the cleaning operation, otherwise the spark will enlarge the die diameter about 0.002 in. in 1 or 2 seconds.

The die is placed with the orifice up on the brass block, *B*, and the sharpened electrode is lowered to within approximately 1 mm of the orifice. When about 40 v are applied to the primary circuit, a spark will pass through the die cone from the electrode. An application of the spark for 2 to 3 seconds will usually remove the dirt. The spark may, however, pass around the die if the die is badly plugged. In this case the die is inverted, and the electrode is lowered into the primary cone. By thus shortening the path for the spark through the secondary cone, the die will be cleaned by reapplying the spark.

3. Drilling Time

The primary cone is drilled by the above procedure in about 3 hr, of which ½ hr is required for electrical spotting and fore-drilling and the remainder for mechanical coning. The secondary cone is formed in 1¼ to 2 hr, including the time required for a 30-minute drilling with NaCl. Back relief is obtained with a 5-minute drilling with NaCl. The total time required to cone and drill a die is therefore approximately 5 hr.

Considerable variation exists in the time required to finish dies. Those needing but a small amount of blending and polishing may be finished in 2 or less hours; others may require as many as 10 hr to obtain a satisfactory finish. In general, 10 hr is about the average time for drilling and finishing a 0.0006- to 0.0012-in. die.

The actual man-hours taken by the die maker to produce small dies will, however, be much

less because all operations except the 30 minutes for high-voltage drilling of the primary cone and the 5 minutes for electrolytic drilling of the back relief may be performed in multiple. One operator can electrolytically drill 6 or more dies simultaneously or can attend 10 or more spindles on the coning and polishing machine for coning and finishing operations. The time required to drill and finish small dies on a production basis should not greatly exceed 2 man-hours.

Neither spotting or fore-drilling by the high-voltage method nor electrolytic drilling of the secondary cone requires special skill or long training of the operator. Most die makers have produced excellent dies after 4 or 5 hr of instruction in the electrical methods by members of the Bureau's Interferometry Section.

4. Quality of the Dies

Cones produced by either high-voltage or electrolytic drilling give no evidence of added strain to the surrounding diamond when examined under polarized light, whereas the material underlying the facets and primary and exit cones shows severe strain and minute fractures when these elements are produced by bruting. Strain to a lesser degree results from mechanical drilling and, although its magnitude decreases with reduced load on the needle and size of diamond powder used, it is still present in mechanically drilled secondary cones. Frequent failure by chipping at the intersection of secondary and exit cones of dies so drilled is ascribed to weakening of the material by the mechanical treatment. Likewise, rapid wear of some dies at their initial size may be attributed to disruption of material underlying the working surfaces of the dies that has not been removed by sufficient polishing.

Operations that tend to injure the diamond are avoided whenever possible at the Bureau. Facets are cut on a flat rotating lap rather than by bruting, and care is taken to avoid excessive loads on the needle while coning the primary cone after electrical fore-drilling. Electrolytically drilled secondary cones are usually quite round, have no drilling rings and, consequently, can be rounded and give a high polish with grade 4 diamond powder. Back relief is obtained by electrolytic drilling. Examination of a large number of dies when coördinated with their wire-drawing records indicated that the finish given a die is of great importance. Therefore, careful attention is paid to the finish of electrically drilled dies. For these reasons, National Bureau of Standards dies should wear as well, particularly at their initial size, as the best mechanically produced dies.

The performance of a die at a given size is measured by the quantity of wire that it draws within a specified tolerance of size and quality of the wire. It depends upon many variables, including the composition of the wire, condition of the wire as it reaches the die, drawing rate, amount of reduction, and other less determinate conditions. After a die wears out-of-round or to a greater diameter than the tolerance permits, it is polished to the next larger size at which the manufacturer wishes to draw wire. This procedure is repeated until the diamond fails by fracture or is no longer usable as a die. Several wire manufacturers are coöperating with this Bureau to determine the performance of 50 National Bureau of Standards dies at their initial diameter and, progressively, through the range of larger diameters until failure occurs. Although the reports submitted thus far are rather meager, the data indicate that an equal or appreciably greater amount of wire is obtained with the National Bureau of Standards dies than is obtained under the same drawing conditions with mechanically drilled dies.

5. Orientation of the Die Axis

Attempts of previous investigators to establish a preferred orientation of the die axis with respect to the crystal axes of the diamond have been somewhat inconclusive. Bureau dies submitted to each of the wire manufacturers included those drilled perpendicular to octahedron, dodecahedron, and cube faces respectively. Test reports thus far received are not sufficiently extensive to indicate a definite superiority of performance for any of these three orientations. The diameter of dies drilled perpendicular to the dodecahedron, face enlarges more rapidly during the polishing operation than those drilled perpendicular to either cube or octahedron faces; it remains to be proved, however, that the rate of increase in diameter by polishing is a reliable accelerated test for comparing die performance.

6. Procedure for Making Exit-Cone Dies

Flat-back dies, see figure 1, B, and figure 14, A, were developed at the Bureau to eliminate failure

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by chipping of the diamond which usually occurs when the bearing intersects the drilled or bruted surface of the exit cone. Furthermore, unless the axis of the exit cone coincides with the axis of the secondary cone, the bearing will intersect the side of the exit cone giving a die that will produce curly wire. This is not true with plane back dies because the secondary cone axis will always be normal to the back surface.

It has been stated that the spherical exit cone gives greater strength to the die. Considering the large size of the exit sphere relative to the small size of the die orifice, the secondary cone for all practical purposes intersects a plane surface. In view of the low breaking strength of a 0.001-in. wire, the small force exerted on the diamond in drawing wire of this size will doubtless be absorbed by that portion of the diamond which is immediately adjacent to the die cone.

In making exit cone dies it is customary either to first drill primary and exit cones and then open by drilling the secondary cone, or to first drill primary and secondary cones and then open by drilling or bruting the exit cone. In either case fractures are almost certain to be produced around the orifice.

While the performance of plane back dies is excellent, most wire manufacturers conservatively prefer to purchase the customary exit cone type (see fig. 1, A, and fig. 14, B). The advantages of the electrical drilling methods, however, apply equally well to the production of this latter type. In this case, after the primary cone is completed, the exit sphere is drilled to within 0.006 in. of the apex of the primary cone. The secondary cone is then drilled electrolytically.

With either type of die it is imperative to produce a well polished relief or countersink of from 0.0005 to 0.001 in. in depth at the orifice to reduce chipping to a minimum.

IX. Conclusion

Electrical drilling greatly reduces the production time for diamond wire-drawing dies less than 0.0015 in. in diameter. Most of the 100 or more hours required to drill and finish a 0.001 in. die by mechanical processes is spent in drilling the small secondary cone. This can be electrically drilled in from 1 to 2 hours. A further saving in time is effected when primary and exit cones are spotted and pilot-drilled electrically. As the necessary mechanical operations and the electrolytic drilling of the secondary cone can be performed in multiple, the labor required to drill and finish dies is reduced accordingly and does not greatly exceed 2 man-hours a die. Service reports from wire manufacturers show that electrically drilled dies give excellent performance.

Equipment for electrical drilling is inexpensive and the drilling technic is simple, thereby making the work less tedious and eliminating the extreme skill required to drill small dies by mechanical methods.

A satisfying development of the present investigation is that domestic die makers are now able to produce economically an adequate supply of small diamond dies in the critical range of 0.0004 to 0.002 in. in diameter.

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National Bureau of Standards

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Effect of Artificial Aging on Tensile Properties and Resistance to Corrosion of 24S–T Aluminum Alloy

By Hugh L. Logan, Harold Hessing, and Harold E. Francis [1]

The effect of aging commercial 24S–T aluminum alloy sheet, for various periods at 350°, 375°, 385° and 400° F, on its tensile properties and resistance to corrosion was determined. Aging for 3 hours at 385° F produced an increase in yield strength of about 25 percent above an initial value of about 50,000 lb/in.², an increase in tensile strength of about 3 percent above an initial value of 70,000 lb/in.², and a decrease to about one-third of the initial elongation of 17 to 18 percent. Approximately the same values for these properties were obtained by aging the material for 20 hours at 350° F, 5 hours at 375° F, or 1½ hours at 400° F. Materials aged 3 to 10 hours at 385° F and 6 to 12 hours at 375° F were generally immune to stress-corrosion cracking and were no more severely damaged in corrosive media, $NaCl+H_2O_2$ solution or marine atmosphere, than the commercially heat-treated material exposed without artificial aging.

I. Introduction

Various authors have reported that the yield strength of heat-treated and strained 24S–T aluminum alloy sheet can be appreciably increased by aging at 350° to 400° F. However, it has also been shown that heating this alloy may increase its susceptibility to intercrystalline corrosion.

Authors [1, 2] [2] who have reported that the yield strength of the heat-treated and strained alloy can be increased as much as 50 percent by aging at temperatures of 350° to 400° F, also found that the ultimate tensile strength was increased 5 to 10 percent by this same treatment. Slow cooling of the 24S–T aluminum alloy from the solution heat-treating temperature [3], or aging of duralumin at temperatures of 135° C (275° F) and 200° C (392° F) [4], have been shown to markedly increase the susceptibility of these materials to intercrystalline corrosion. This occurs almost entirely at, or immediately adjacent to, the grain boundaries, and may be very damaging to the ultimate tensile strength and ductility (as measured by percent elongation) of the material. Furthermore, it has been shown [5] that the application of stress to a material, susceptible to intercrystalline corrosion and exposed in a corrosive medium, accelerates the corrosive attack. On the other hand, the corrosion damage to material, susceptible only to the pitting type of corrosion at the surface, is not appreciably increased by the application of stress to the material.

It was the purpose of this project, undertaken at the request of and with financial assistance from the Bureau of Aeronautics, Navy Department, to determine if it was possible to heat treat the material to take advantage of the increased yield strength without increasing the danger of intercrystalline corrosion.

II. Materials

Commercially heat-treated 24S–T aluminum alloy sheet is normally strained approximately 1 percent after solution heat treatment in order to produce a flat product. The specimens used in this investigation were prepared from two commercial 24S–T aluminum alloy flat sheets each 48 in. by 144 in. by 0.064 in. The sheets were obtained from different sources. They will be

[1] Formerly at the National Bureau of Standards.

[2] Figures in brackets indicate the literature references at the end of this paper.

referred to below as sheet *A* and sheet *B*. The chemical compositions of the two sheets were:

	Sheet *A*	Sheet *B*
	Percent	*Percent*
Copper	4. 5	4. 3
Magnesium	1. 5	1. 4
Manganese	0. 6	0. 6
Iron	. 25	. 43
Silicon	. 19	. 27

In addition to the above elements, both sheets contained traces of calcium, chromium, gallium, lead, nickel, silver, tin, titanium, and vanadium, as determined spectroscopically. Sheet *B* also contained a trace of zinc.

III. Testing Procedure

The method of test consisted of aging the materials for various times at temperatures of 350°, 375°, 385°, and 400° F and subsequently determining their tensile properties as aged and after exposure in various corrosive media. The term "aging" as used hereafter will refer to artificial or elevated-temperature aging and not to the spontaneous aging that takes place at room temperature after the solution heat treatment of the 24S alloy. Specimens were exposed for 24 hours, stressed in tension to three-fourths of the yield strength, in a sodium chloride-hydrogen peroxide solution (NaCl, 57 g; H_2O_2 (30%) 10 ml; H_2O, 990 ml) [6] in the laboratory. Immersion in this solution has proved to be a satisfactory accelerated test to indicate the type of corrosion that may be expected to develop in aluminum alloys of the duralumin type in marine exposure [7]. Specimens were also exposed in the weather unstressed and stressed, as indicated above, and unstressed in tidewater, all at the Naval Air Station, Hampton Roads, Va. The changes in tensile properties, particularly the ultimate tensile strength and percentage elongation, resulting from exposure of the materials in the corroding media were taken as a measure of the corrosion damage. The type of corrosive attack was determined by metallographic examination of the exposed material.

Prior to the elevated-temperature aging treatment, most of the material was machined into standard ASTM ½-in. reduced-section tensile specimens. Machined tensile specimens were artificially aged in an oven that had been brought to the desired temperature before it was charged with specimens. The oven was provided with a blower for air circulation and thermostatic control to ±3°F. A period of 8 to 12 minutes was required to bring the thermostat element back to the desired temperature after placing the specimens in the oven. The aging period was measured from that time, on the assumption that the specimens, which were well separated and small in volume, reached the oven temperature along with the thermostat element.

Panels 6 in. by 14 in. for exposure (unstressed) in a marine atmosphere and for intermittent immersion in tidewater were cut from the original sheet materials, 0.064 in. thick, described above, and were aged for various periods in a tempering furnace at 385°±10°F. At the end of all aging treatments, the specimens were quenched into tap water at room temperature.

All tensile tests were made with a hydraulic type of testing machine having a 5,000-pound load range. The cross-head speed was approximately 0.05 in. per minute. Yield strengths were obtained from load-strain diagrams drawn by a Templin type high-magnification stress-strain recorder. The values reported for the tensile properties are the averages obtained from three or more specimens.

Stress-corrosion tests were made on specimens loaded axially by means of simple lever systems. The stress-corrosion rack used in the laboratory for testing many of these specimens is shown in figure 1.

The cells were of Pyrex glass, 60 mm outside diameter, fitted into grooves in the Bakelite disks at the top and bottom. Breakage of the cylinders was reduced and watertight seals were made by using rubber gaskets between the glass and Bakelite. Rubber stoppers (molded by the Rubber Section of the National Bureau of Standards) containing rectangular slots slightly smaller than the grip ends of the specimens fitted into tapered holes in the lower Bakelite disks. Use of these stoppers facilitated the insertion and removal of specimens and at the same time prevented leakage of the corroding solution.

Three specimens for each aging period, for specimens aged at 350°, 385°, or 400° F, were immersed in the solution at room temperature

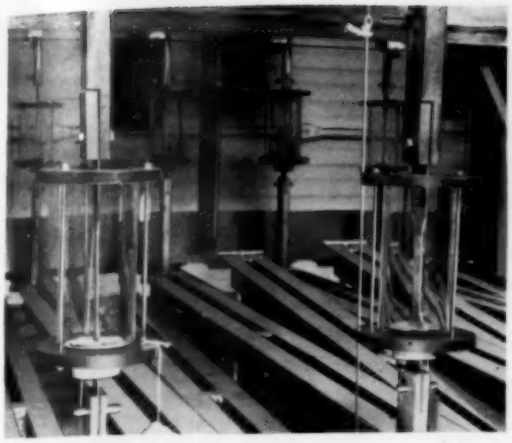

FIGURE 1.—*Stress-corrosion rack with cells in place for tests in the* $NaCl+H_2O_2$ *solution.*

Specimens loaded axially by means of lever systems. Cord (right) connects knife switch and lever so that circuit to solenoid counter is opened if specimen breaks.

under stresses equal to three-fourths of the yield strength of the particular specimens under test. Room temperature was between 70° and 85° F. In order to eliminate temperature as a factor in the corrosion testing, and also to evaluate the effect of stress as a factor in corrosion damage, two sets of specimens for each aging period at 375° F were immersed in the $NaCl+H_2O_2$ solution at a temperature of 95°±1° F; one set of specimens was unstressed, the second set was stressed to three-fourths of the yield strength. The temperature 95° F was selected, on recommendation of the Bureau of Aeronautics, because salt-spray corrosion data are obtained at that temperature.

To supplement the laboratory stress-corrosion tests, tensile specimens aged at 375° and 385° F were exposed in a marine atmosphere at the Naval Air Station, Hampton Roads, Va. Tensile specimens aged at 385° F were anodized before being exposed; specimens aged at 375° F were exposed with no surface treatment other than degreasing. The racks used in exposing the specimens are shown in figure 2, and fixtures for holding specimens and the specimens themselves are illustrated in figure 3. The device for measuring times to failure of the specimens is shown in figure 4. Loads were applied by means of lever systems and weights. Specimens were loaded to produce stresses, in the reduced sections, approximately

FIGURE 2.—*Stress-corrosion racks, Naval Air Station, Hampton Roads, Va.*

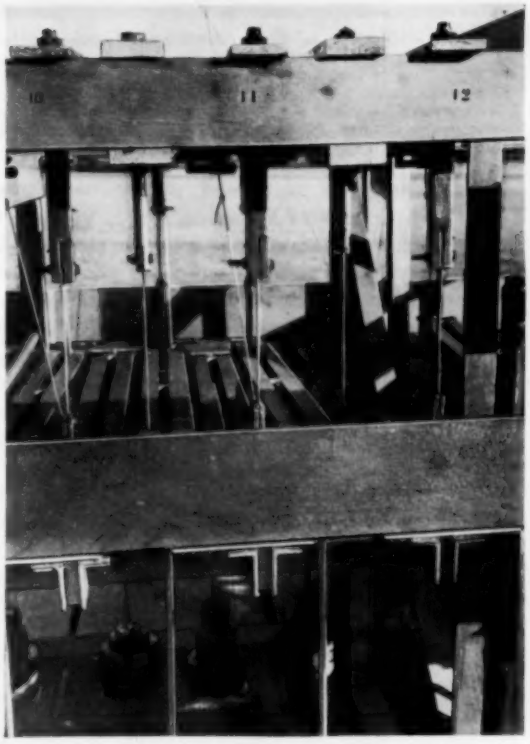

FIGURE 3.—*Stressed and unstressed specimens in marine-atmosphere stress-corrosion rack.*

equal to three-fourths of the yield strengths, and were exposed for approximately 6 weeks. Specimens aged at 375° F were also exposed to the marine atmosphere unstressed, but with conditions otherwise identical with those for the stressed specimens.

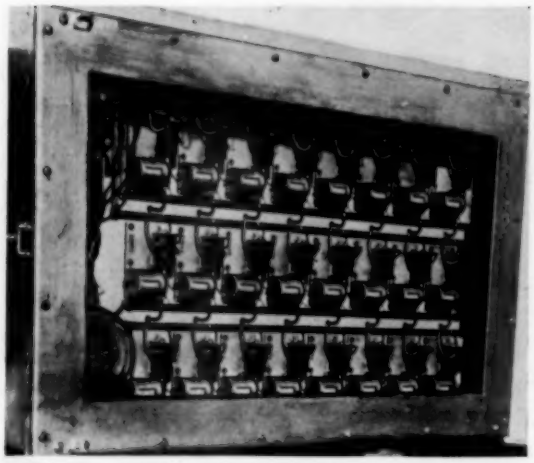

FIGURE 4.—*Electric solenoid counters and time switch (lower left).*

Counters are connected in series with knife switches located above individual specimens (see fig. 3). Counters are actuated once each 6 min (by electric time switch) until knife switch is opened upon failure of specimen, i. e., time to failure of specimen is recorded in 0.1 -hr unit.

The panels for unstressed weather exposure and tidewater tests at Hampton Roads were heat treated and were then cut into two parts, each 3 in. by 14 in. One part of each panel was exposed to intermittent immersion in tidewater for 14 days; the other part was exposed to marine weather for 1 year. The test sites and methods of mounting specimens have been described in a report of another investigation [8]. After exposure, the panels were returned to the Bureau, and their tensile properties determined.

The type and extent of corrosive attack on the materials were determined, after their removal from the corrosive media, by metallographic examination of one or more coupons from each set of the corroded specimens.

IV. Results

The tensile properties of the commercially heat-treated material, without elevated-temperature aging, as determined from specimens taken parallel and transversely to the direction of rolling, and hereafter designated parallel and transverse respectively, were:

Material	Yield strength [1]		Ultimate tensile strength		Elongation in 2 in.	
	Parallel	Transverse	Parallel	Transverse	Parallel	Transverse
	lb/in.²	*lb/in.²*	*lb/in.²*	*lb/in.²*	*Percent*	*Percent*
A	54,300	47,600	71,700	70,700	17	18
B	50,500	44,400	67,300	67,200	18	18½

[1] 0.2 percent offset from the modulus line.

Specimens taken parallel to the direction of rolling were aged at 350° F for periods of time from 2 to 24 hours; at 375° F for periods of 2 to 12 hours; at 385° F for 8 minutes to 12 hours; and at 400° F for 1 to 6 hours. Specimens taken transversely to the direction of rolling were aged for periods of time from 1 to 8 hours at 385° F. The results of the aging treatments and corrosion tests are given in tables 1 to 6 and are shown graphically in figures 5 to 20, inclusive. Standard deviations for yield strengths, etc., given in the tables were computed from averages of ranges [9].

TABLE 1.—*Effect of aging period at 385° F on tensile properties and resistance to corrosion of 0.064-in.-gage commercial 24S–T aluminum-alloy sheet, lot A*

Aging time at 385° F	Tensile properties of aged material			Stress in corroding medium	Tensile properties after 24 hr. under stress in $NaCl+H_2O_2$ solution			Tensile properties after 6 weeks under stress in marine atmosphere [2]		
	Yield strength [1]	Ultimate tensile strength	Elongation in 2 in.		Yield strength	Ultimate tensile strength	Elongation in 2 in.	Yield strength	Ultimate tensile strength	Elongation in 2 in.
PARALLEL SPECIMENS										
Hours	*lb/in.²*	*lb/in.²*	*Percent*		*lb/in.²*	*lb/in.²*	*Percent*	*lb/in.²*	*lb/in.²*	*Percent*
0	54,300	71,700	17		40,500	46,800	53,600	3	52,800	70,700	12
3/4	51,300	70,400	17½		38,500	42,200	45,700	2½	.....	.....	.....
¼	49,100	70,200	19		36,800	42,300	47,300	3	.....	.....	.....
½	55,700	70,900	17		41,700	44,900	48,300	3	.....	.....	.....
1	62,000	72,200	12½		47,600	56,100	61,800	4	63,000	70,200	8½
2	66,700	73,800	8½		50,700	59,500	63,800	3½	67,200	74,200	5
2½	67,400	74,100	8½		.....	.....	.....	.....	.....	.....	.....
3	68,600	73,400	7		51,200	61,400	66,000	4½	65,600	72,500	6
4	67,000	72,700	7½		50,100	61,100	65,000	4	66,700	72,900	6
5	67,000	73,300	6½		50,700	62,000	65,800	4	.....	.....	.....
6	65,500	72,200	6		48,800	57,600	62,500	3½	62,000	70,700	7
7	64,500	71,000	6½		48,400	59,100	64,800	4	.....	.....	.....
8	63,800	71,400	7		48,000	57,500	63,800	3	62,600	71,200	7
10	63,100	70,900	6½		47,900	57,400	63,800	3½	.....	.....	.....
12	64,300	71,200	6½		47,900	58,200	63,900	3½	64,700	70,800	6½
Standard deviation.[3]	1,130	725	0.70	.....	955	1,425	0.50	1,350	1,140	0.80
TRANSVERSE SPECIMENS										
0	47,600	70,700	18		35,700	42,800	47,800	2	.....	.....	.....
1	57,800	72,500	13		45,300	51,700	55,300	2½	.....	.....	.....
2	63,000	71,800	8		47,300	56,800	62,500	3½	.....	.....	.....
2½	63,400	70,100	6		47,600	58,200	62,100	2½	.....	.....	.....
3	65,900	72,300	6½		49,300	59,500	64,100	3½	.....	.....	.....
4	65,700	71,900	6½		49,300	57,000	60,000	2½	.....	.....	.....
5	66,100	72,400	6		49,600	58,700	61,800	2½	.....	.....	.....
6	64,700	70,900	6		48,200	58,100	61,000	2	.....	.....	.....
8	62,800	70,300	6½		47,200	.....	60,800	2½	.....	.....	.....
Standard deviation.[3]	945	415	0.60	.....	1,090	1,600	0.55	.....	.....	.....

[1] 0.2% offset from modulus line.

[2] Material inserted in rack 12/23/44, removed 2/2/45. These specimens anodized before exposure.

[3] The standard deviation was determined by dividing the average range by 1.693; see Simon, "Engineer's manual of statistical methods", p. 138. Range equals maximum value minus minimum value.

TABLE 2.—*Effect of aging period at 385° F on tensile properties and resistance to corrosion of 0.064-in.-gage 24S–T commercial aluminum alloy, lot B*

Aging period at 385° F	Tensile properties of aged material			Stress in corroding medium	Tensile properties after 24 hr in $NaCl+H_2O_2$ solution under stress			Tensile properties after 6 weeks under stress in marine atmosphere		
	Yield strength	Ultimate tensile strength	Elongation in 2 in.		Yield strength	Ultimate tensile strength	Elongation in 2 in.	Yield strength	Ultimate tensile strength	Elongation in 2 in.
PARALLEL SPECIMENS										
Hours	*lb/in.²*	*lb/in.²*	*Percent*	*lb/in.²*	*lb/in.²*	*lb/in.²*	*Percent*	*lb/in.²*	*lb/in.²*	*Percent*
0	50,500	67,300	18	38,300	47,100	58,800	7	49,500	65,700	9
¾s	48,200	66,700	18	36,900	41,700	46,900	2½	.....	.....	.....
¼	47,600	66,200	19	36,800	41,100	47,600	3	.....	.....	.....
½	50,500	68,300	18	37,000	43,700	49,500	3	.....	.....	.....
1	51,400	66,100	16	40,300	45,200	50,400	3	56,500	61,900	3½
1½	57,600	68,100	11	44,000	51,100	57,600	3½	.....	.....	.....
2	62,000	68,900	8	46,900	55,100	59,900	4	63,300	68,400	5½
2½	62,100	69,000	7½	.....	.....	.....	.....	.....	.....	.....
3	62,500	68,400	7	47,000	55,500	60,500	3½	63,500	68,300	5
4	61,900	67,900	7	46,300	55,900	60,600	4	63,400	69,600	5½
5	59,000	67,500	6½	44,500	53,700	58,900	3	.....	.....	.....
6	61,700	67,600	6½	46,300	56,100	60,400	3	61,800	67,600	5½
7	58,800	66,600	6½	44,100	53,500	58,500	2½	.....	.....	.....
8	60,100	66,600	6	45,800	54,700	58,600	2½	59,900	66,900	6
10	59,900	67,100	6	45,000	53,800	59,000	3	.....	.....	.....
12	57,000	65,100	6½	43,900	50,700	55,100	2½	58,900	66,700	5½
Standard deviation.	910	605	0.4	.....	690	960	0.45	515	1,260	1.4
TRANSVERSE SPECIMENS										
0	44,400	67,200	18½	33,700	43,400	59,800	6	.....	.....	.....
1	50,100	67,600	15	38,000	44,900	51,600	3	.....	.....	.....
2	59,900	68,100	7½	45,400	53,800	60,000	4	.....	.....	.....
2½	56,300	65,700	6½	42,500	52,900	59,400	3½	.....	.....	.....
3	62,900	70,200	6½	47,600	54,500	60,000	4	.....	.....	.....
4	61,400	68,000	6½	46,600	54,900	60,400	3½	.....	.....	.....
5	61,100	67,800	6½	46,300	55,300	60,900	3½	.....	.....	.....
6	59,300	66,800	6	44,800	53,300	59,100	3	.....	.....	.....
8	61,000	68,200	6	45,700	.....	59,600	2½	.....	.....	.....
Standard deviation.	610	505	1.0	.....	575	860	0.6	.....	.....	.....

TABLE 3.—*Tensile properties of material before and after exposure in tidewater for 2 weeks or in a marine atmosphere for 1 year*

Aging period at 385° F.	Properties of aged material (unexposed)			Properties of material after 14 days' exposure in tidewater			Properties of material after 1 year's exposure in marine atmosphere		
	Yield strength	Ultimate tensile strength	Elongation in 2 in.	Yield strength	Ultimate tensile strength	Elongation in 2 in.	Yield strength	Ultimate tensile strength	Elongation in 2 in.
				A MATERIAL					
Hours	*lb/in.²*	*lb/in.²*	*Percent*	*lb/in.²*	*lb/in.²*	*Percent*	*lb/in.²*	*lb/in.²*	*Percent*
0	54,300	71,700	17	54,200	70,800	15½	54,600	70,700	16½
1	62,000	72,200	12½	54,900	68,900	10½	44,500	49,500	5
2	66,700	73,800	8½	61,500	72,900	10	60,900	70,400	9
2½	67,400	74,100	8½	65,100	74,200	9½	63,200	71,700	8
3	68,600	73,400	7	66,400	73,700	8½	65,600	73,200	8
4	67,000	72,700	7½	67,300	73,800	7	66,100	73,300	7
5	67,000	73,300	6½	68,200	73,400	6	67,000	72,700	6
6	65,500	72,200	6	67,800	72,800	4½	66,900	72,500	5½
8	63,800	71,400	7	65,100	70,900	5½	63,500	70,500	6
Standard deviation.	1,050	750	0.55	335	530	0.85	1,070	1,550	0.70
				B MATERIAL					
0	50,500	67,300	18	51,100	67,700	16	50,700	67,500	15
1	51,400	66,100	16	51,400	64,900	8½	50,800	63,600	10
2	62,000	68,900	8	55,500	65,700	6½	54,700	66,100	8½
2½	62,100	69,000	7½	58,500	64,800	3	55,700	66,100	7
3	62,500	68,400	7	60,100	67,100	5	58,700	66,800	6
4	61,900	67,900	7	62,400	66,900	4½	61,700	68,300	6
5	61,100	68,200	7	62,900	66,700	4½	62,200	68,100	5½
6	61,700	67,600	6½	61,000	65,200	3	61,000	67,600	4
8	60,100	66,600	6	60,600	66,000	4	60,400	66,700	5½
Standard deviation.	490	520	0.40	610	1,085	0.95	790	270	0.80

TABLE 4.—*Effect of aging period at 375° F on parallel tensile properties and resistance to corrosion of 0.064-in.-gage commercial 24S–T aluminum alloy*

Aging period at 375° F	Tensile properties of aged material			Stress in corroding medium	Tensile properties after 24 hr in $NaCl+H_2O_2$ solution			Tensile properties after 6 weeks in marine atmosphere [1]		
	Yield strength	Ultimate tensile strength	Elongation in 2 in.		Yield strength	Ultimate tensile strength	Elongation in 2 in.	Yield strength	Ultimate tensile strength	Elongation in 2 in.
				A MATERIAL						
Hours	*lb/in.²*	*lb/in.²*	*Percent*	*lb/in.²*	*lb/in.²*	*lb/in.²*	*Percent*	*lb/in.²*	*lb/in.²*	*Percent*
0	54,300	71,700	17	40,500	47,600	55,300	4	54,700	71,900	14
0	54,300	71,700	17	0	50,900	65,800	10½	54,000	71,600	15½
2	62,800	75,000	15½	51,300	56,000	60,100	4	-------	-------	-------
2	62,800	75,000	15½	0	58,000	64,300	7½	-------	-------	-------
3	65,100	74,300	11	-------	-------	-------	-------	-------	-------	-------
4	69,300	74,200	6½	52,000	63,000	68,600	5½	67,400	72,700	6
4	69,300	74,200	6½	0	64,600	69,700	7	69,000	74,400	5½
5	69,500	73,800	7½	-------	-------	-------	-------	-------	-------	-------
6	67,600	73,200	7½	48 to 50,000	62,800	68,200	5½	66,000	72,000	6
6	67,600	73,200	7½	0	60,600	66,700	5	64,300	71,700	6
7	67,700	73,600	7	-------	-------	-------	-------	-------	-------	-------
8	67,600	73,400	6	50,800	62,100	67,700	5½	66,700	72,200	6
8	67,600	73,400	6	0	62,300	67,500	5	66,200	72,000	5
10	64,500	71,600	6½	-------	-------	-------	-------	-------	-------	-------
12	64,000	71,300	6½	47,900	59,100	65,900	5½	61,500	69,900	5½
12	64,000	71,300	6½	0	59,800	65,900	5	62,900	70,700	6
Standard deviation	500	495	0.40	Stressed	1,395	1,715	1.0	1,275	970	1.1
				Unstressed	1,165	825	1.0	1,735	545	0.80
				B MATERIAL						
0	50,500	67,300	18	37,900	43,600	55,000	6	49,200	61,300	8½
0	50,500	67,300	18	0	46,300	61,700	9½	48,400	66,700	15
2	56,200	67,900	13	42,150	47,800	55,800	5	-------	-------	-------
2	56,200	67,900	13	0	46,800	58,200	8	-------	-------	-------
3	59,200	68,800	10½	-------	-------	-------	-------	-------	-------	-------
4	63,200	69,600	7½	47,400	50,100	63,200	3½	62,500	67,100	4
4	63,200	69,600	7½	0	55,700	63,300	6	61,700	67,300	4½
5	63,300	68,900	7½	-------	-------	-------	-------	-------	-------	-------
6	62,900	69,400	6½	47,200	57,700	62,900	4	60,500	67,000	4
6	62,900	69,400	6½	0	57,300	63,200	5	62,000	68,400	5
8	60,300	67,400	6	45,300	56,800	61,800	3½	59,600	66,500	4
8	60,300	67,400	6	0	56,600	61,500	4	59,900	66,000	4
10	62,100	68,300	6½	-------	-------	-------	-------	-------	-------	-------
12	60,800	67,500	6	45,300	56,200	61,000	4½	61,300	66,300	5
12	60,800	67,500	6	0	55,800	61,000	4½	59,600	65,000	4
Standard deviation	620	395	0.60	Stressed	885	600	0.60	1,040	1,030	1.0
				Unstressed	660	550	1.2	1,450	1,005	0.40

[1] Material inserted in rack 3/17/45, removed 4/28/45.

TABLE 5.—*Effect of aging period at 350° F on parallel properties and resistance to corrosion of 0.064-in.-gage commercial 24S-T aluminum alloy*

Aging period at 350° F	Tensile properties of aged material			Stress in corroding medium	Tensile properties after 24 hr in $NaCl+H_2O_2$ solution		
	Yield strength	Ultimate tensile strength	Elongation in 2 in.		Yield strength	Ultimate tensile strength	Elongation in 2 in.
				A MATERIAL			
Hours	*lb/in.²*	*lb/in.²*	*Percent*	*lb/in.²*	*lb/in.²*	*lb/in.²*	*Percent*
0	54,300	71,700	17	40,500	46,800	53,600	3
2	55,600	72,000	17	41,700	<45,300	[1]<48,300	2½
4	57,200	72,500	17½	42,900	45,700	49,200	3
8	66,800	74,700	9½	50,100	56,100	62,000	3
16	69,600	74,000	6½	52,200	61,400	65,800	3
24	69,600	73,900	6	52,000	61,000	65,600	3
Standard deviation.	1,215	400	0.6	.....	1,160	2,620	0.5
				B MATERIAL			
0	50,500	67,300	18	37,900	47,100	58,800	7
2	51,300	67,700	17½	38,500	41,000	44,800	2½
4	53,300	68,600	17	40,000	41,700	45,600	3
8	61,500	70,200	9	46,100	53,500	57,900	2½
16	63,400	69,200	6	47,600	56,500	61,000	3½
24	63,500	69,700	6½	47,300	56,800	61,100	3
Standard deviation.	985	490	0.6	.....	1,110	1,200	0.4

[1] Two of these specimens broke in corroding medium.

TABLE 6.—*Effect of aging period at 400° F. on parallel tensile properties and resistance to corrosion of 0.064-in.-gage commercial 24S-T aluminum alloy*

Aging period at 400° F	Tensile properties of aged material			Stress in corroding medium	Tensile properties after 24 hr in $NaCl+H_2O_2$ solution		
	Yield strength	Ultimate tensile strength	Elongation in 2 in.		Yield strength	Ultimate tensile strength	Elongation in 2 in.
				A MATERIAL			
Hours	*lb/in.²*	*lb/in.²*	*Percent*	*lb/in.²*	*lb/in.²*	*lb/in.²*	*Percent*
0	54,300	71,700	17	40,500	46,800	53,600	3
1	67,700	73,200	6½	51,100	62,200	66,700	4
2	65,900	72,400	7	49,900	59,500	64,500	3½
3	65,600	72,100	6½	49,500	60,800	65,600	4
4	65,300	72,300	6½	49,000	58,800	63,700	3½
6	63,500	71,500	6½	47,400	56,400	62,100	3
Standard deviation.	660	700	0.25	--------	720	1,665	0.5
				B MATERIAL			
0	50,500	67,300	18	37,900	47,100	58,800	7
1	59,800	69,500	9	46,000	52,300	59,000	4
2	62,400	69,200	6½	49,000	53,700	58,700	3½
3	59,600	67,000	6½	45,800	52,800	58,000	3
4	59,100	67,000	6	44,500	51,800	56,400	3
6	58,600	66,300	6	43,900	51,800	56,100	2½
Standard deviation.	1,030	510	0.4	--------	1,275	1,045	0.6

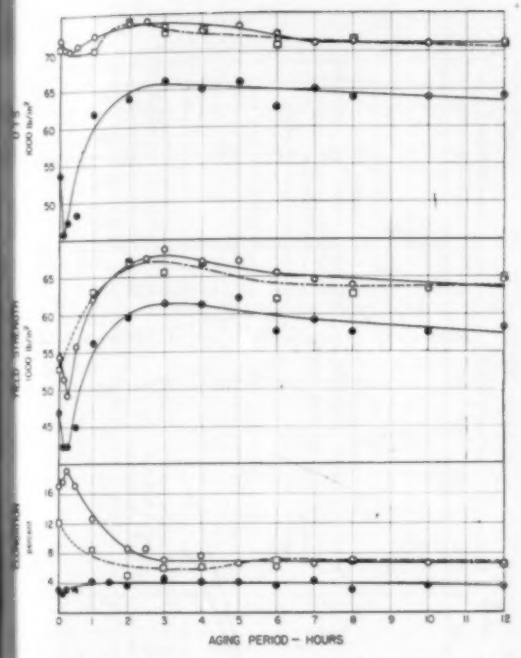

FIGURE 5.—*Tensile properties of parallel specimens of A material, aged at 385° F, before and after exposure (anodized) to a marine atmosphere for 6 weeks and in the* $NaCl+H_2O_2$ *solution without surface protection for 24 hr.*

○, Uncorroded; □, exposed in marine atmosphere, stressed to three-fourths of yield strength; ●, corroded in $NaCl+H_2O_2$ solution, stressed to three-fourths of yield strength.

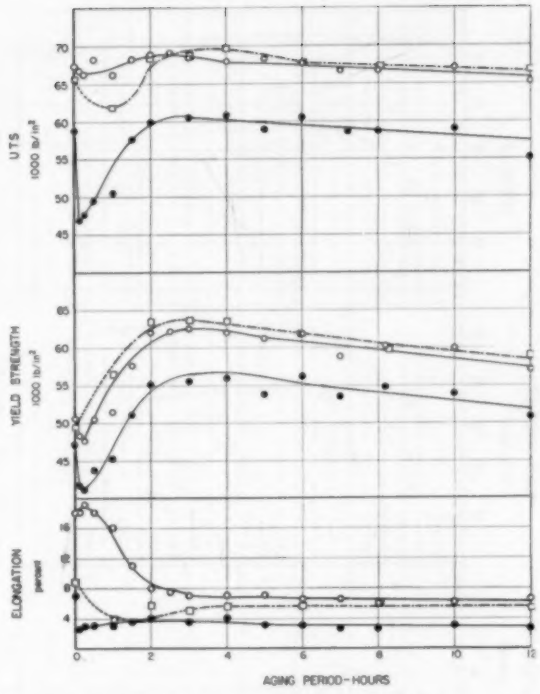

FIGURE 6.—*Tensile properties of parallel specimens of B material, aged at 385° F, before and after exposure (anodized) to a marine atmosphere for 6 weeks and in the* $NaCl+H_2O_2$ *solution without surface protection for 24 hr.*

○, Uncorroded; □, exposed in marine atmosphere, stressed to three-fourths of yield strength; ●, corroded in $NaCl+H_2O_2$ solution, stressed to three-fourths of yield strength.

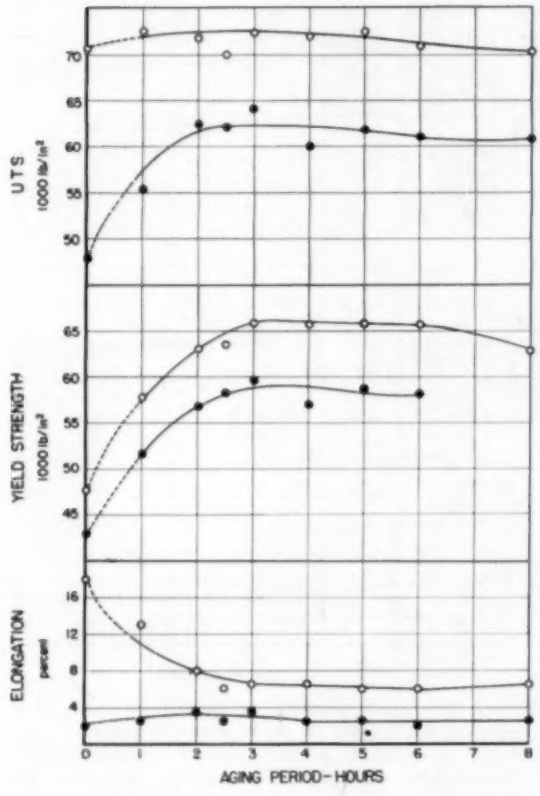

FIGURE 7.—*Tensile properties of transverse specimens of A material, aged at 385° F, before and after exposure for 24 hr in the* $NaCl+H_2O_2$ *solution.*

○, Uncorroded; ●, corroded in $NaCl+H_2O_2$ solution, stressed to three-fourths of yield strength.

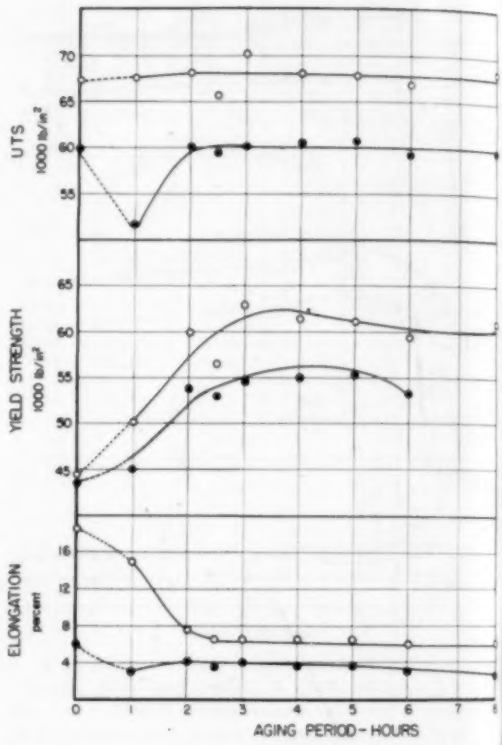

FIGURE 8.—*Tensile properties of transverse specimens of B material, aged at 385° F, before and after exposure for 24 hr in the* $NaCl+H_2O_2$ *solution.*

○, Uncorroded; ●, corroded in $NaCl+H_2O_2$ solution, stressed to three-fourths of yield strength.

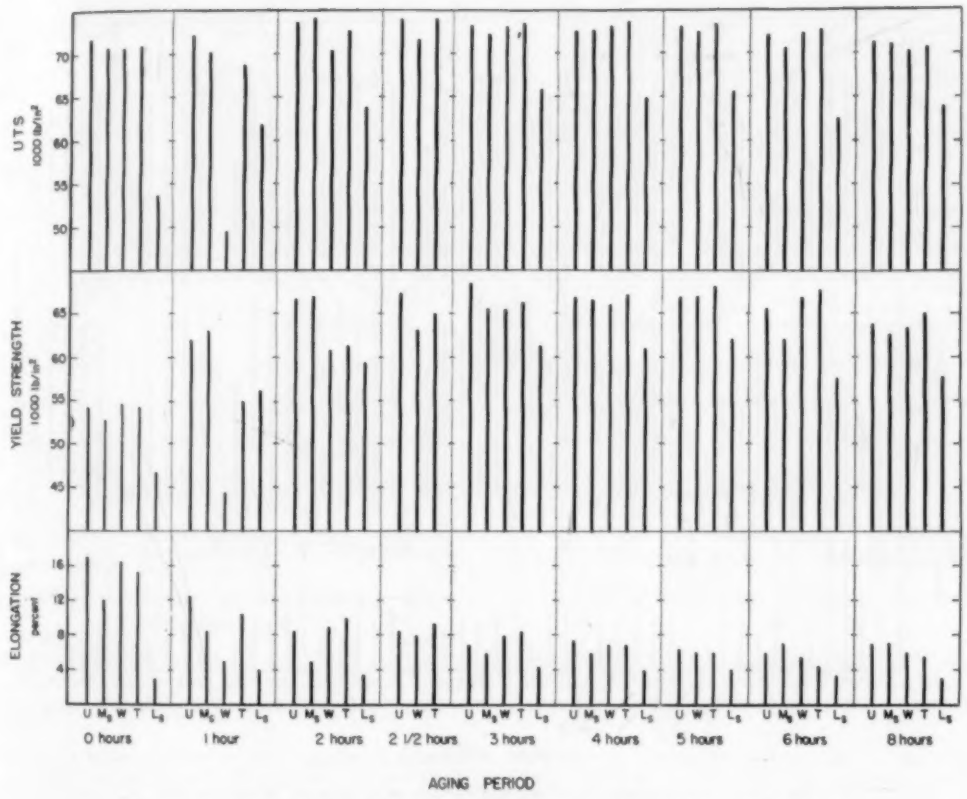

FIGURE 9.—*Tensile properties of parallel specimens of A material aged at 385° F.*

U, As aged; M_s, exposed, stressed to three fourths of yield strength, in marine atmosphere for 6 weeks; *W*, exposed, unstressed, in marine atmosphere for 1 yr; *T*, exposed, unstressed, to intermittent immersion in tidewater for 14 days; L_s, immersed, stressed to three fourths of yield strength, in the NaCl+H_2O_2 solution in the laboratory for 24 hr. Specimens M_s were anodized prior to exposure; all other specimens were exposed without surface protection.

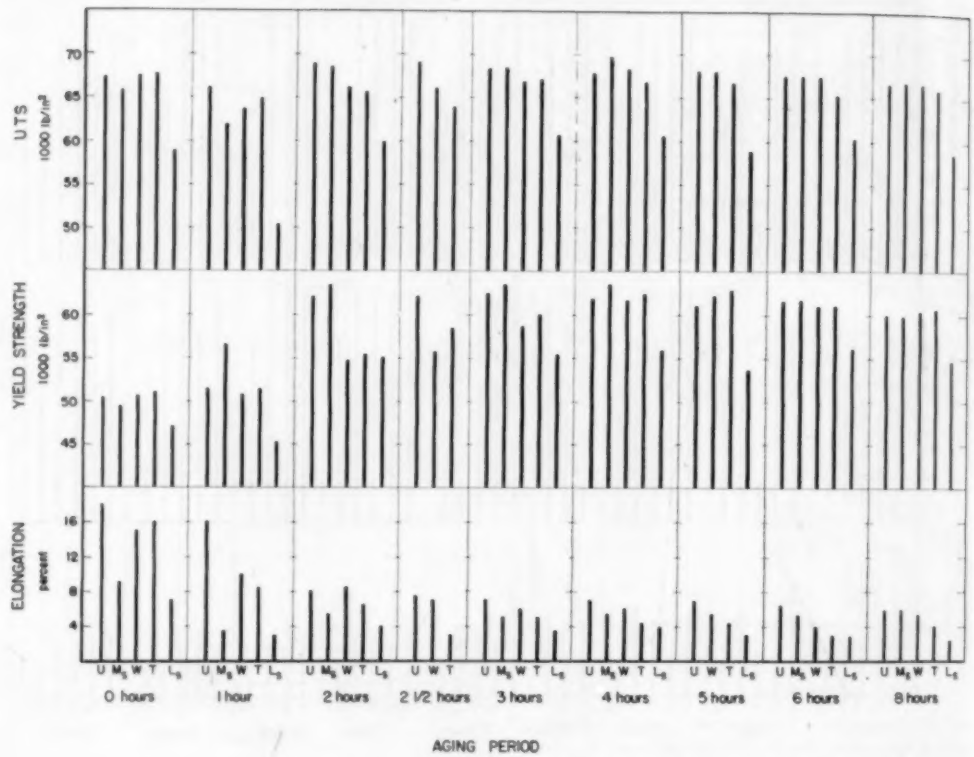

FIGURE 10.—*Tensile properties of parallel specimens of B material aged at 385° F.*

U, As aged; *M*, exposed, stressed to three fourths of yield strength, in marine atmosphere for 6 weeks; *W*, exposed, unstressed, in marine atmosphere for 1 yr; *T*, exposed, unstressed, to intermittent immersion in tidewater for 14 days; *L*, immersed, stressed to three fourths of yield strength, in the NaCl+H2O2 solution in laboratory for 24 hr. Specimens *M* were anodized prior to exposure, all other specimens were exposed without surface protection.

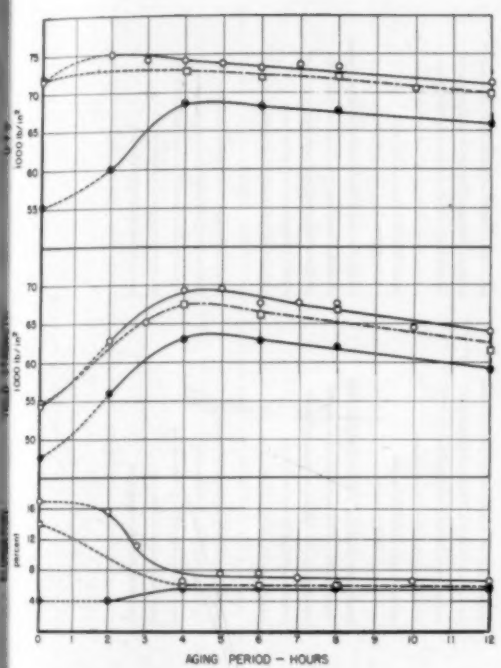

FIGURE 11.—*Tensile properties of parallel A specimens, aged at 375° F, before and after exposure in a marine atmosphere for 6 weeks and in the* $NaCl+H_2O_2$ *solution for 24 hr.*

○, Uncorroded; □, exposed in marine atmosphere, stressed to three-fourths of yield strength; ●, corroded in $NaCl+H_2O_2$ solution, stressed to three-fourths of yield strength.

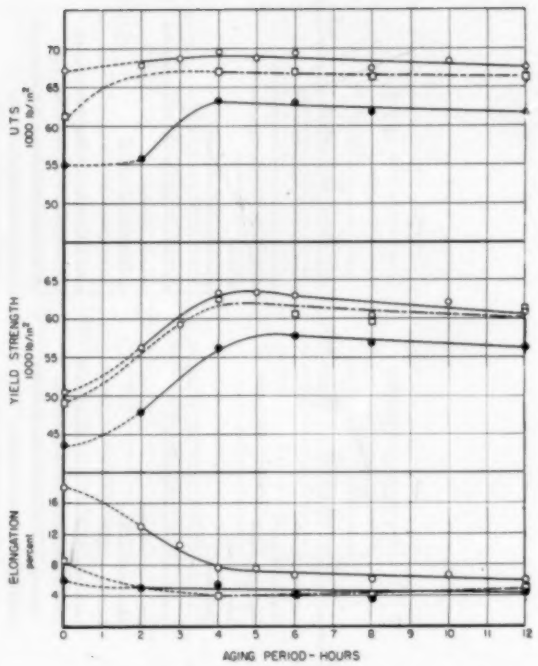

FIGURE 12.—*Tensile properties of parallel B specimens, aged at 375° F, before and after exposure in a marine atmosphere for 6 weeks and in the* $NaCl+H_2O_2$ *solution for 24 hr.*

○, Uncorroded; □, exposed in marine atmosphere, stressed to three-fourths of yield strength; ●, corroded in $NaCl+H_2O_2$ solution, stressed to three-fourths of yield strength.

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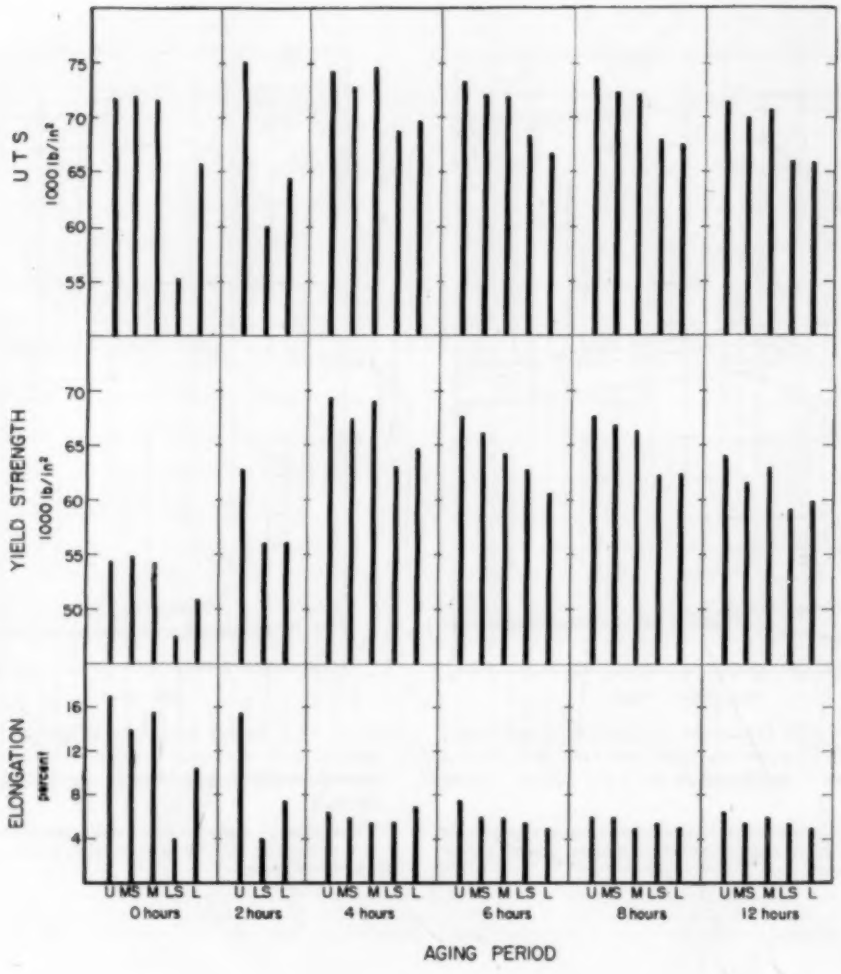

FIGURE 13.—*Effect of stress and corrosion on tensile properties of parallel A specimens aged at 375° F.*

U, as aged; *MS*, corrodent, marine atmosphere, stressed to three-fourths of yield strength; *M*, corrodent, marine atmosphere, stress=0; *LS*, corrodent, $NaCl+H_2O_2$, stressed to three-fourths of yield strength; *L*, corrodent, $NaCl+H_2O_2$, stress=0.

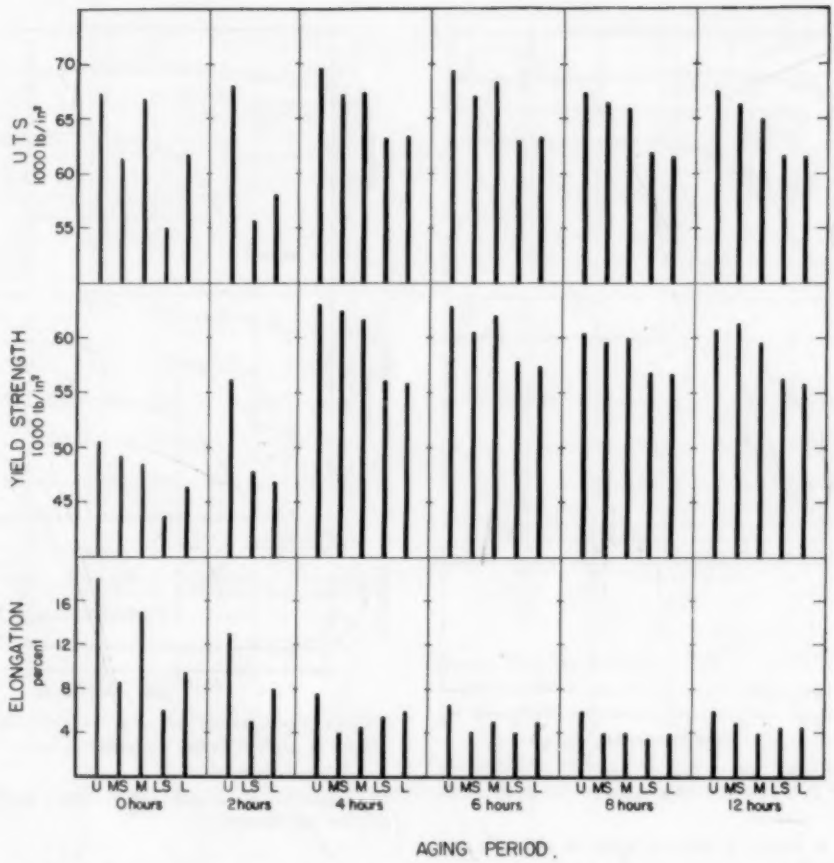

FIGURE 14.—*Effect of stress and corrosion on tensile properties of parallel B specimens aged at 375° F.*

U, as aged; *MS*, corrodent, marine atmosphere, stressed to three-fourths of yield strength; *M*, corrodent, marine atmosphere, stress=0; *LS*, corrodent, $NaCl+H_2O_2$, stressed to three-fourths of yield strength; *L*, corrodent, $NaCl+H_2O_2$, stress=0.

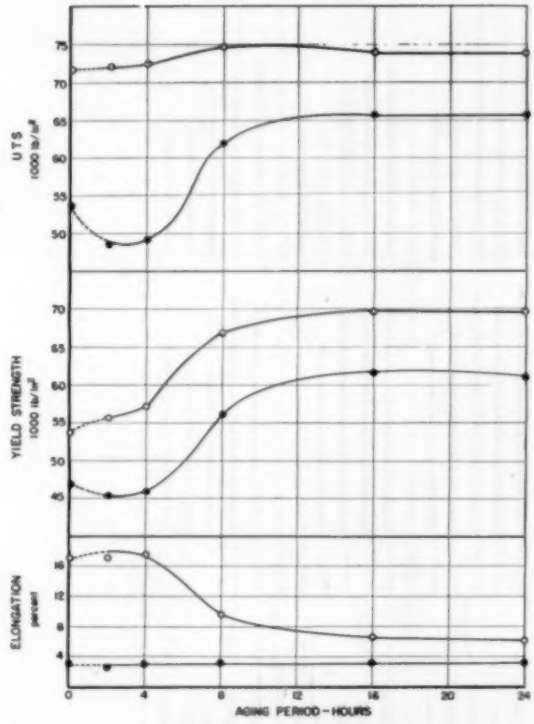

FIGURE 15.—*Tensile properties of parallel A specimens, aged at 350° F, before and after exposure for 24 hr in the* $NaCl+H_2O_2$ *solution.*

○, Uncorroded; ●, corroded in $NaCl+H_2O_2$ solution, stressed to three-fourths of yield strength.

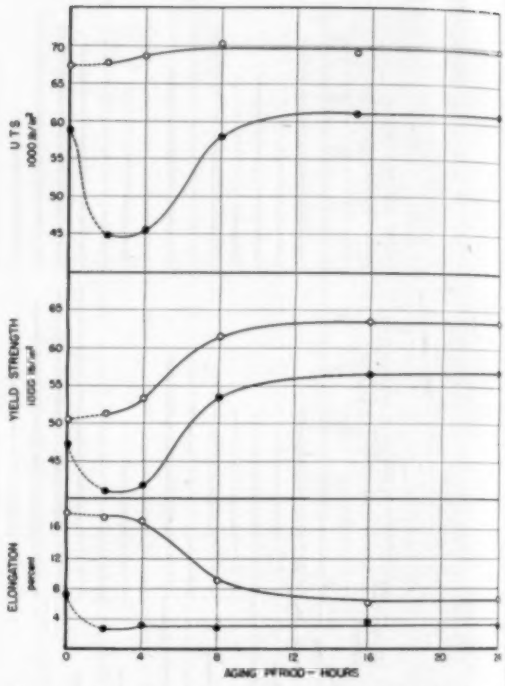

FIGURE 16.—*Tensile properties of parallel B specimens, aged at 350° F, before and after exposure for 24 hr in the* $NaCl+H_2O_2$ *solution.*

○, Uncorroded; ●, corroded in $NaCl+H_2O_2$ solution, stressed to three-fourths of yield strength.

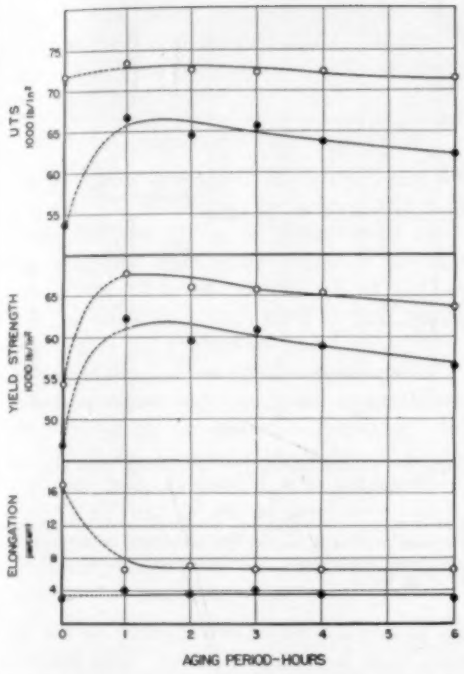

FIGURE 17.—*Tensile properties of parallel A specimens, aged at 400° F, before and after exposure for 24 hr in the* $NaCl+H_2O_2$ *solution.*

○, Uncorroded; ●, corroded in $NaCl+H_2O_2$ solution, stressed to three-fourths of yield strength.

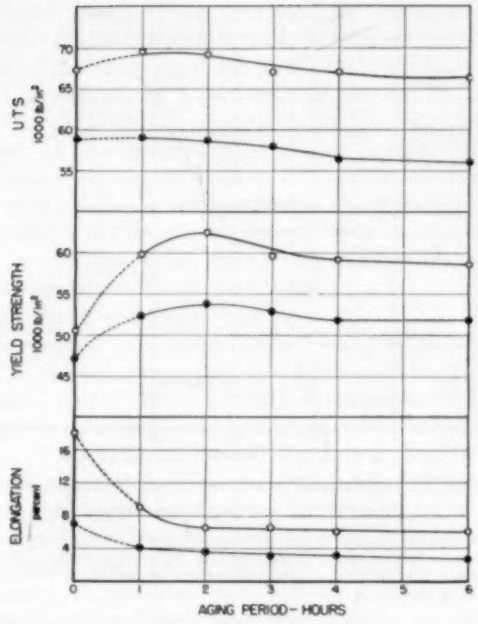

FIGURE 18.—*Tensile properties of parallel B specimens, aged at 400° F, before and after exposure for 24 hr in the* $NaCl+H_2O_2$ *solution.*

○, Uncorroded; ●, corroded in $NaCl+H_2O_2$ solution, stressed to three-fourths of yield strength.

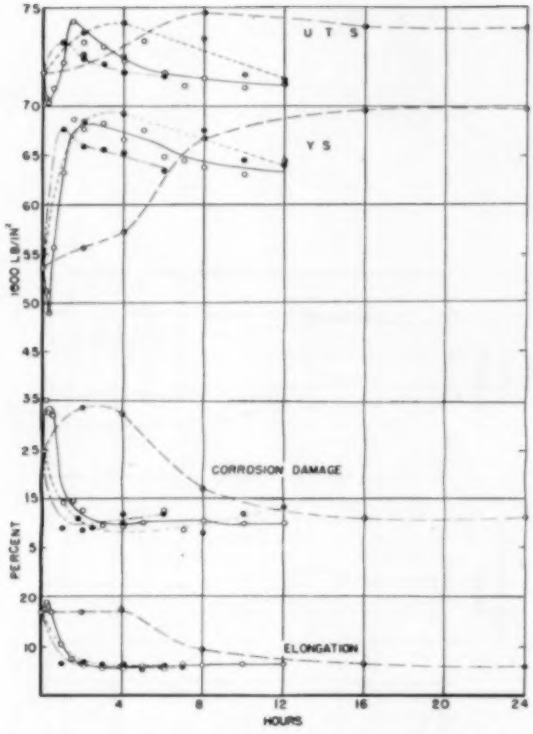

FIGURE 19.—*Relationship between aging time and tensile properties of parallel A specimens.*

Corrosion damage = percentage loss in ultimate tensile strength of specimens exposed for 24 hr in the $NaCl+H_2O_2$ solution under stress equal to three-fourths of yield strength. Aging temperature: ◑, 350° F; ⊕, 375° F; ○, 385° F; ●, 400° F.

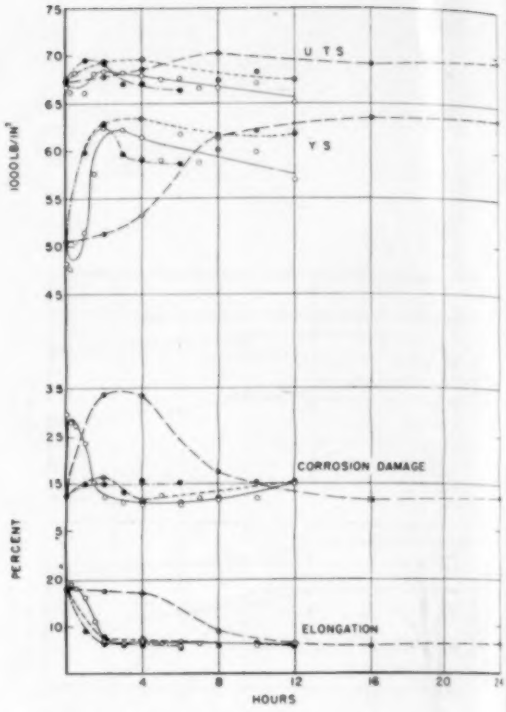

FIGURE 20.—*Relationship between aging time and tensile properties of parallel B specimens.*

Corrosion damage = percentage loss in ultimate tensile strength of specimens exposed for 24 hr in the $NaCl+H_2O_2$ solution under stress equal to three-fourths of yield strength. Aging temperature: ◑, 350° F; ⊕, 375° F; ○, 385° F; ●, 400° F.

1. Effect of Aging on Tensile Properties

The aging period necessary to obtain the maximum values for tensile and yield strengths varied from approximately 20 hr at 350° F to 1½ hr at 400° F.

(a) Materials Aged at 385° F

The results for parallel specimens are shown in figures 5 and 6 and in tables 1 and 2. Aging of the materials for periods of 8 and 15 minutes reduced the ultimate tensile and yield strengths and increased the percentage elongations. For longer aging periods the yield and ultimate tensile strengths increased and reached maximum values, for 2½ to 3 hr aging, as follows: Ultimate tensile strength 74,100 lb/in.² and 69,000 lb/in.², for the *A* and *B* lots of material respectively; the maximum yield strengths were 68,600 lb/in.² and 62,500 lb/in.², respectively. The values for these properties decreased slightly as the aging periods were increased to 12 hr. The percentage elongation decreased as the aging period was increased beyond 15 minutes and became constant at 6½ to 7 percent, after aging periods of 3 to 6 hours.

Computation of the standard deviations for aging periods that may be commercially important (2½ to 6 hr, inclusive) gave values somewhat smaller than those obtained from the averages of the ranges of all the aging periods. The standard deviations over this range for the yield strengths were 810 lb/in.² and 565 lb/in.²; for the ultimate tensile strengths, 390 lb/in.² and 590 lb/in.²; and for the percentage elongations, 0.3 and 0.25 percent for the *A* and *B* materials, respectively.

The results obtained on transverse specimens are summarized in figures 7 and 8 and in tables 1 and 2. The maximum yield strengths were

obtained by aging for 3 hr. The ultimate tensile strengths were increased 2 to 4½ percent by aging at this temperature. The original yield strengths of the transverse specimens were lower than those of the parallel specimens, and the yield and tensile strengths of the transverse *A* specimens after aging periods of 3 hr or longer were generally 2,000 to 3,000 lb/in.^{2} lower than those of the parallel specimens aged for the same periods. However, the values of the tensile properties of the *B* material were approximately the same, after aging periods of 3 hr or more, whether the specimens had been taken transversely or parallel to the direction of rolling.

(b) Materials aged at 350°, 375°, and 400° F

Data for aging periods at 375°, 350°, and 400° F are shown graphically in figures 11 to 18, inclusive, and are given in tables 4, 5, and 6. Rather complete data were obtained for aging periods of 2 to 12 hr at 375° F, but at 350° and 400° F the specimens were aged at only enough periods to give the general shape of the curves of tensile properties plotted against aging periods.

Maximum values for the yield strength were obtained by aging the materials for from 4 to 6 hr at 375° F and from 16 to 24 hr at 350° F. No specimens were aged for a period of less than 1 hr at 400 ° F; data on the *A* specimens indicate that the maximum yield strength for this material might possibly have been obtained by aging this material for less than 1 hr.

Irrespective of the aging temperatures there was a maximum increase of approximately 3 percent in ultimate tensile strengths of parallel specimens over that of the unaged material and 25 percent in yield strengths. The increases in yield and ultimate tensile strengths were accompanied by decreases of about 60 percent in the values for percentage elongation.

Standard deviations were approximately the same whether the values of all the specimens aged at 375° F or only those aged for periods of 4 to 12 hr were considered. Standard deviations for all the data were computed for specimens aged at 350° and 400° F.

2. Susceptibility of Materials to Corrosion

It was found that, in general, specimens aged for relatively short periods of time were the most severely damaged in the corroding media; as the aging period was increased to produce the maximum yield strength, the materials became less susceptible to corrosion and stress-corrosion cracking. Further aging, up to four times the period necessary to produce maximum properties for specimens aged at 385° F, did not appreciably change the resistance of the specimens to corrosion.

(a) Materials Aged at 385° F

In the laboratory exposures of stressed specimens in $NaCl+H_2O_2$ solution, the changes in ultimate tensile strength and percentage elongation of materials aged for 8, 15, and 30 minutes, and subsequently immersed for 24 hr in the $NaCl+H_2O_2$ solution, were much greater than those of specimens aged 1 hr or longer. The resistance of the material to the combined action of stress and corrosion continued to increase as the aging period was increased from 1 to 3 hr. Thereafter, there was little if any change in corrosion resistance with increased aging periods. (See figs. 5 to 10 and tables 1 to 3.)

Specimens of commercially heat-treated material and specimens that had been aged for 1, 2, 3, 4, 6, 8, and 12 hr at 385° F were stressed to three-fourths of the yield strength and exposed in the marine atmosphere. Unaged specimens and specimens aged for 1 hr were more severely damaged than specimens aged for longer periods prior to exposure. Material aged 3 hr or longer was, in general, less severely damaged after 6 weeks of exposure under stress in the marine atmosphere than the unaged material exposed under the same conditions.

The results obtained with unstressed panels exposed to the weather in a marine atmosphere and to alternate immersion in tidewater were in agreement with those given above. The greatest losses in tensile strength and ductility (see figs. 9 and 10 and table 3) occurred in materials aged less than 3 hr. In the weather exposure, specimens of both materials aged 3 hr or longer were generally less severely damaged than the unaged materials. This was also true of the *A* material in tidewater, but the unaged *B* material proved, in general, to be slightly more resistant to corrosion in tidewater than any of the aged *B* material.

Examination of the microstructures of specimens aged for various periods of time and subsequently exposed in the various corrosive media showed that material aged 8 minutes or longer

was susceptible to intercrystalline corrosion in some degree. Specimens aged 8 minutes to 1 hr and subsequently exposed to the $NaCl+H_2O_2$ solution contained severe intercrystalline corrosion and the beginnings of stress corrosion cracks, as shown in figure 21, A. A material aged for a period of 1 hr and exposed unstressed in a marine atmosphere for 1 year contained more severe intercrystalline corrosion than was found in any other material examined (fig. 21, B). With longer aging periods, the areas of intercrystalline attack became less general and more spotty (fig. 21, C). For aging periods of 8 to 12 hr, the intercrystalline corrosion was associated with pitting (fig. 21, D).

(b) Effect of Aging at 375° F

Unaged specimens and specimens that had been aged for 2 hr were more severely damaged when exposed under stress in the $NaCl+H_2O_2$ solution than similar specimens exposed under identical conditions except that they were not stressed. The effect of stress in increasing corrosion damage was less pronounced in specimens aged 4 hr than in specimens aged for the shorter periods and there was generally little difference in corrosion damage to specimens aged 6 hr or longer whether the specimens had been exposed stressed or unstressed in the corroding medium.

The losses in tensile strength and ductility of materials aged 6 hr or longer and subsequently exposed for 6 weeks in a marine atmosphere were generally no greater than those for the commercially heat treated but unaged material.

(c) Effect of Aging at 350° F

Metallographic examinations of specimens after their removal from the $NaCl+H_2O_2$ solution indicated that all the aged material contained intercrystalline corrosion in some degree. Specimens aged for periods up to 12 hr contained more severe intercrystalline corrosion than specimens aged for longer periods of time.

(d) Effect of Aging at 400° F

Material aged 2 hr or longer contained only traces of intercrystalline corrosion on metallographic examination of specimens after their their removal from the $NaCl+H_2O_2$ corroding solution.

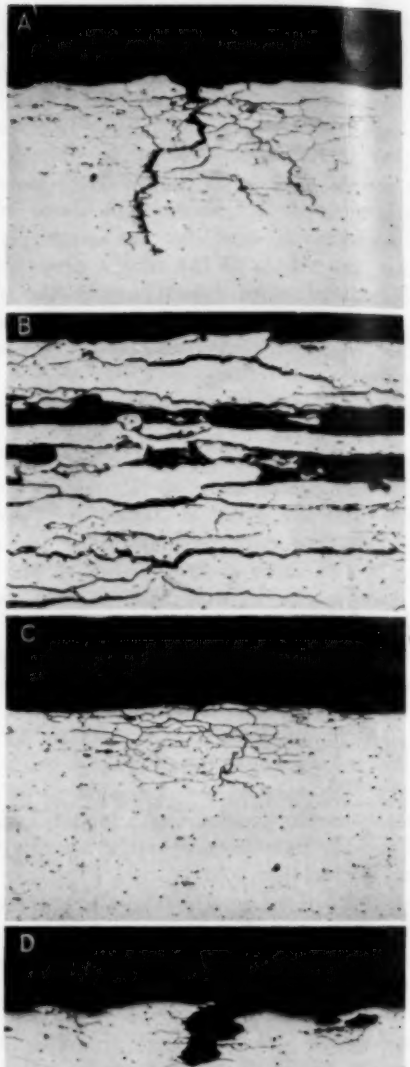

FIGURE 21.—*Types of corrosion.*

A, Severe, intercrystalline, and beginning of stress corrosion crack typical of corrosion produced in material aged about 30 minutes at 385° F. Unetched. × 100; *B*, material aged 1 hr and exposed (unstressed) for 1 yr in marine atmosphere. Unetched. × 100; *C*, less severe intercrystalline than that shown in *A* and typical of corrosion found in material aged for longer periods (3 to 4 hr at 385° F) prior to exposure. Unetched. × 100; *D*, intercrystalline extending out from pits. Typical of corrosion found in material aged for 8 to 10 hr at 385° F prior to exposure. Unetched. × 100.

V. Discussion of results

The changes in tensile properties with the aging periods, for the four temperatures used are shown in figures 19 and 20. As was indicated above, approximately the same maximum tensile properties were obtained for the various aging temperatures used between 350° and 400° F. However, the aging period necessary to produce the maximum yield strength decreased with increased aging temperatures. In many metallurgical phenomena, particularly where diffusion may be involved, it is found that a linear relation holds between the logarithm of the time and the reciprocal of the absolute temperature. Accordingly the reciprocals of the aging temperatures in degrees Kelvin were plotted as ordinates, and the aging times necessary to obtain maximum yield strengths were plotted on a logarithmic scale, as abscissas in figure 22. The plotted points lie approximately on a straight line represented by an equation of the form

$$t = Ae^{-\frac{B}{K}},$$

where t is the aging period in hours, K the absolute temperature in degrees K, and A and B constants whose values are

$A = 3.85 \times 10^{-19}$ hr, $B = -20.4 \times 10^3$ degrees K.

The aging temperatures in degrees Fahrenheit were also plotted against the aging periods for maximum yield strength as shown in figure 22. A curve was obtained similar to that shown by Mozley [1] but with a somewhat different slope. Better correlation was evident, between the curve (computed by the method of least squares) and the plotted points, when aging periods were plotted against the reciprocals of the absolute temperatures than against the Fahrenheit temperatures. The Bravais-Pearson coefficients of correlation were 0.999 and 0.866, respectively, for the two curves.

The 24S–T alloy transferred without delay from the solution heat-treating furnace to the quenching bath and cooled at a sufficiently high rate [3] to room temperature is immune to the very damaging intercrystalline type of corrosion and is susceptible only to the more innocuous pitting type of corrosion. It is generally considered that the susceptibility of the material to

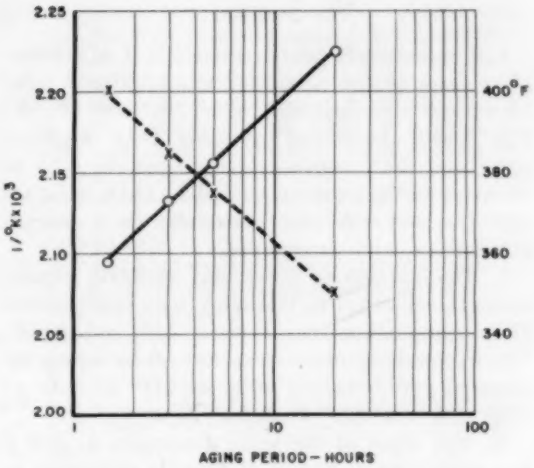

FIGURE 22.—*Relationship between aging temperature and aging period necessary to produce maximum yield strengths.*

Rising line represents reciprocals of absolute temperatures, and falling line represents temperature in degrees F. ○, 1/°K–time; ×, °F–time.

corrosion damage is increased by elevated temperature aging as well as by failure to satisfy the above conditions for rapid cooling. The results of the corrosion and stress-corrosion tests in the laboratory, in a marine atmosphere and in tidewater were significant in that they show: (a) that material that had been aged for a period sufficient to produce maximum mechanical properties was, in general, no more susceptible to corrosion damage than the commercially heat-treated material exposed without elevated-temperature aging, (b) that the application of stresses, equal to three-fourths of the yield strength, did not appreciably increase corrosion damage, over that to unstressed material, for specimens aged 6 hr or longer at 375° F. Stressed specimens of materials exposed after an aging period of 2 hr at 375° F, and specimens exposed with no elevated-temperature aging were generally much more severely damaged than the comparable specimens exposed unstressed in the corroding media, (c) there were no data to indicate that material aged at one temperature, in the range 350° to 400° F, sufficiently long to obtain the maximum physical properties was more resistant to corrosion than material aged at another temperature to the same condition.

VI. Summary

1. Commercially heat-treated 24S–T aluminum alloy sheet (0.064 in. thick) was artificially aged for various periods at 350°, 375°, 385°, and 400° F. The tensile properties resulting from artificial aging and the resistance of the aged material to stress-corrosion cracking in $NaCl+H_2O_2$ solution and (for some of the materials) in a marine atmosphere, were determined.

2. The maximum yield and ultimate tensile strengths obtained in this alloy were independent of the aging temperature between 350° and 400° F. The optimum results were obtained by aging the material approximately 20 hr at 350° F, 5 hr at 375° F, 3 hr at 385° F, and 1½ hr at 400° F.

3. The effect of the aging treatment at 385°F was more pronounced on the tensile properties in a transverse direction than on those in a direction parallel to the direction of rolling. The yield strength of the transverse specimens of the commercially heat-treated material was increased approximately 40 percent above an initial value of about 45,000 lb/in.^{2}, and the ultimate tensile strength approximately 3 percent above an initial value of about 70,000 lb/in.^{2} The percentage elongation was reduced to about one-third of the initial value of 18. Effects of the same magnitude were observed for the parallel specimens, except that the yield strength was increased only about 25 percent above an initial value of about 50,000 lb/in^2.

4. Corrosion damage was measured by losses in elongation and ultimate tensile strength. Elevated-temperature aging of materials for short periods compared to those necessary to obtain the maximum mechanical properties, increased the susceptibility of the material to corrosion. However, for aging periods sufficiently long [3] to produce maximum physical properties, the resistance to corrosion of the artificially aged material was generally at least equal to that of the commercially heat-treated material exposed without elevated temperature aging. The ultimate tensile strengths of specimens exposed under stress in the sodium chloride-hydrogen peroxide solution were reduced as much as 30 to 35 percent for material aged for short periods of time. The reduction was only 10 to 15 percent for specimens aged for periods sufficiently long to produce maximum tensile properties. The same amount of exposure of unaged material reduced its ultimate tensile strength by 11 to 32 percent.

Losses in tensile strength and ductility of anodized material aged 3 hr or longer at 385° F and exposed for 6 weeks under stress in the marine atmosphere were small; the maximum loss in ultimate tensile strength was 1,500 lb/in.^{2}, a loss which is probably not significant in this case; the maximum loss in ductility was represented by specimens in which the percent elongation was reduced from 7 to 5.

Specimens aged for 6 hr or longer at 375° F and subsequently exposed without surface protection by anodic treatment for 6 weeks in the marine atmosphere were generally no more severely damaged than the commercially heat-treated material exposed without artificial aging. For one lot of unaged material the effect of stress was marked in increasing the corrosion damage; the ultimate tensile strength of the stressed specimens was reduced 9 percent, as the result of 6 weeks of exposure in the marine atmosphere, compared to 1 percent for the unstressed material; the percent elongations on the two sets of specimens were reduced 53 and 17 percent, respectively. However, there was little difference in the corrosion damage to specimens that had been aged 6 hr or more at 375° F whether they were exposed stressed or unstressed in the corroding media.

The maximum losses in tensile strengths and ductilities of unstressed panels, exposed without surface protection to the weather (marine atmosphere for 1 year) or to tidewater (intermittent immersion for 14 days), were found in specimens aged 1 to 2½ hr (at 385° F).

5. Intercrystalline corrosion in some degree was found in all of the aged materials on examination after exposure in any of the corroding media. The intercrystalline corrosion was most severe in specimens aged for short periods of time; as the aging periods were increased to or beyond those necessary to produce the maximum values of yield strength, for the various aging temperatures, the intercrystalline corrosion became less general and less severe than that found in specimens aged for the shorter periods.

[3] In some instances, also for aging periods up to three or four times the minimum necessary to produce maximum physical properties.

The assistance of Houston Babb, Thomas P. Royston, Jr., and Richard C. Rohan; and the cooperation of Willard H. Mutchler and Fred M. Reinhart, of this Bureau; and Lieutenants C. A. Snavely and M. Franklin, of the Naval Air Station, Hampton Roads, Va., in this investigation is gratefully acknowledged.

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Washington, November 22, 1946.

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National Bureau of Standards

Research Paper RP1789
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Cooperative Analysis of a Standard Sample of Natural Gas with the Mass Spectrometer

By Martin Shepherd [1]

The mass spectrometer was used for the analysis of a standard sample of natural gas by laboratories cooperating with Subcommittee VII of Committee D–3 of the American Society for Testing Materials. The results of the cooperative analysis show the reproducibility and, in certain respects, the accuracy of this powerful new apparatus for gas analysis. The heating value and the specific gravity of the sample calculated from the analytical data were compared with the known values.

I. Introduction

This report is the third of a series of cooperative analyses of standard gas samples [2] conducted to furnish basic information for the preparation of standard methods for the analysis of fuel gases. The development of these standards is a task assigned to Subcommittee D–3–VII of the ASTM, and the method of this development has been outlined in two previous reports.[3]

The 20 laboratories that cooperated in the present work were widely distributed geographically, but most of them were associated with the petroleum industry. There was some representation from the chemical industry, but only one college and one Federal bureau participated. Fortunately, both of the companies making the spectrometers used in this series of analyses contributed the services of the instruments in their home laboratories. The cooperating laboratories owned 21 mass spectrometers. Of these, 18 were manufactured by the Consolidated Engineering Corporation and the other three by the Westinghouse Electric Corporation. The Consolidated spectrometer [4] operates with a fixed magnetic field and varying accelerating voltage; the Westinghouse spectrometer [5] reverses this system. The Consolidated instrument produces its spectrogram photographically with a recording oscillograph; the Westinghouse instrument employs a pen-and-ink recorder. However, the basic principle upon which each was built is the same, and the analytical results should be the same. Indeed, it will be observed that results from the two instruments are not widely different, although there were some definite suggestions of individuality. In both types of instruments there were minor variations in design. Two different models of the Consolidated instrument operated with different rates of scan, somewhat different sensitivity, and a slight difference in the system for focusing the ion beam—apparently with no significant difference in the analytical results. The Westinghouse instruments were equipped with linear or log-linear recorders, and one of the three was a laboratory research model, not a production model.

The same freedom from variety noted for the apparatus was true also for the analytical procedures. In general, all of the laboratories followed the procedures for operating, calibrating, and computing prescribed by the manufacturers.

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[2] These samples are not to be confused with the regular standard samples prepared and offered for sale by the National Bureau of Standards. They are mixtures prepared especially for these cooperative analyses and are issued to laboratories cooperating with the American Society for Testing Materials on this project.

[3] Martin Shepherd, Analysis of a standard sample of the carburetted water-gas type by laboratories cooperating with the American Society for Testing Materials, J. Research NBS 36, 313 (1946) RP1704; Analysis of a standard sample of natural gas by laboratories cooperating with the American Society for Testing Materials, J. Research NBS 38, 19 (1947) RP1759.

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Departures from the prescribed course were very few and of such a nature that no significant change was expected or observed. Perhaps the greatest variation was in the calibrating substances used, some of which were obtained from different sources and were not of uniform purity.

Thus, with respect to both apparatus and methods, this series of cooperative analyses was accorded the convenience of standardization which was unofficial but none the less real; and while this may or may not have been a factor in the accuracy achieved, it must have affected the over-all reproducibility.

II. Standard Natural Gas Sample ASTM D–3–VII–3

The preparation of the standard sample of the natural-gas type, identified as ASTM D–3–VII–2, which was used in the cooperative analysis by volumetric chemical methods, has been described in detail in Bureau Research Paper RP1759.[6] The account given in RP1759 will serve to establish the complete history of the present sample, ASTM D–3–VII–3, which was analyzed by the mass spectrometer—as the No. 2 and No. 3 samples were identical. This was not disclosed when No. 3 was issued, and accordingly it was analyzed as a blind sample. In general, it did not find its way into the same laboratories that had performed the chemical analyses. In a few cases, however, the results obtained by the mass spectrometer came under the same reviewing eye as had those obtained by the chemical methods. How many positive correlations were made is not known. In only one case was a puzzled suspicion voiced.

Sample ASTM D–3–VII–3 was issued in the same type of cylinder as that used for the No. 2 sample, and the instructions for transferring it to the spectrometer without contamination were essentially the same as those given for the previous sample (see RP1759). This information will accordingly not be repeated here.

Having thus put chemical and physical methods into direct competition, it is of considerable interest to see what happened. The part of the story concerned with the analysis by the mass spectrometer is given in this paper. (An additional report comparing the chemical and physical analysis is in preparation.)

[6] See footnote 3.

III. Analytical Results

All of the analytical data submitted have been tabulated, together with the average values derived from each laboratory series; but the contemplation of these data for a considerable time would not serve to reveal what may be seen at a glance when these same data are presented in a series of frequency-distribution plots. Accordingly, these plots, which amount to actual pictures of the analytical results, have been chosen as the best method of presentation and what few remarks seem justified have been included in the legends of the corresponding plots.

In the plots each circle represents a value derived from a single determination of the substance whose name appears in the legend. The circles are plotted equidistant on the ordinate corresponding to their values. Thus, the abscissas are values derived from the analyses, and the ordinates indicate the frequency with which these values occur. For example, the lower section of the frequency-distribution plot for methane (fig. 1) shows that one determination gave the value 75.4 percent, two determinations gave 75.5 percent, one gave 76.0 percent, one gave 76.4, four gave 76.7, eight gave 76.8, and so on. The lower section of this plot is marked C+W, and shows all of the 118 determinations of methane made with both the Consolidated and Westinghouse instruments. In the middle section, marked W, the Westinghouse results are separately plotted. The top section shows the averages from each of the laboratories (or perhaps more properly, from each of the instruments, since there were 20 laboratories and 21 instruments). In this section the W values are indicated with open circles.

These conventions are carried throughout the group of plots. In some cases, where relatively few determinations of a component (often actually not in the sample) have been reported, division of the plot into three sections has not been necessary, for there are neither W values nor laboratory averages. With these conventions in mind, the frequency-distribution plots can be studied.

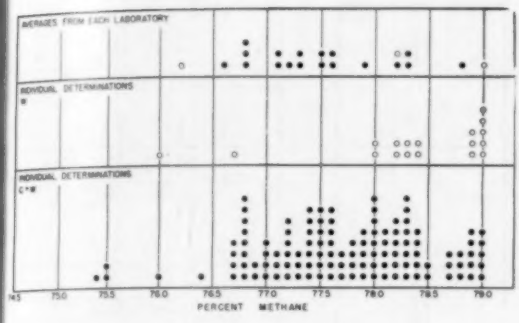

FIGURE 1.—*Frequency-distribution plot for methane.*

All determinations are given in the lower section (C+W), and those made by the W instruments are given separately in the middle section (W). The upper section shows the averages from each of the laboratories. The analyses yielded values over a range of 4.6 percent, although 80 percent of the determinations were confined to a range of 1.8 percent. Within this lesser range, the distribution is fairly even, with no tendency to a greater frequency at any value, and with an arithmetical mean of 77.6±0.5. The mean of the whole group is 77.7, and that of the laboratory averages is 77.5±0.6. Outside values appear in both the W and C determinations. The ± values noted indicate reproducibility expressed as the average absolute deviation from the average given.

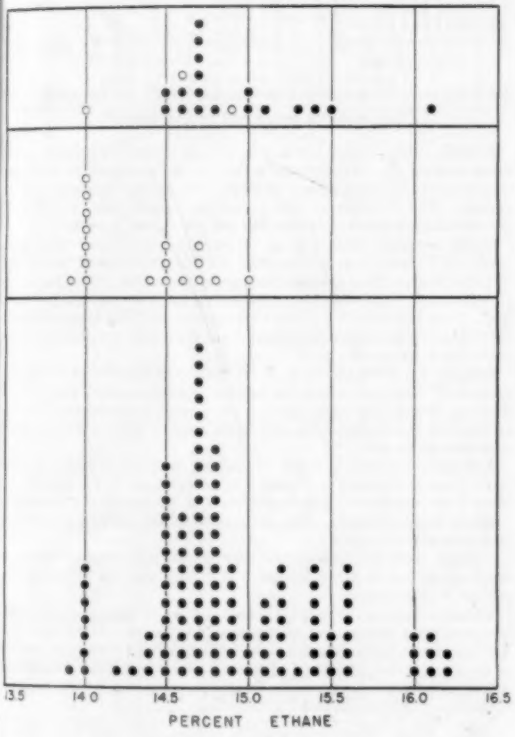

FIGURE 2.—*Frequency-distribution plot for ethane.*

The three sections of the plot follow the same convention used in the plot for methane. The analyses yielded values ranging over 2.3 percent, with a mean value of 14.9. The greatest frequency appears at 14.7 percent. Eighty percent of the determinations are confined within a range of 1.1 percent; the mean of this group is 14.9±0.3. The mean of the laboratory averages, exclusive of the two outside values, is 14.8 ±0.2. Some of the W values are not in agreement with the general group.

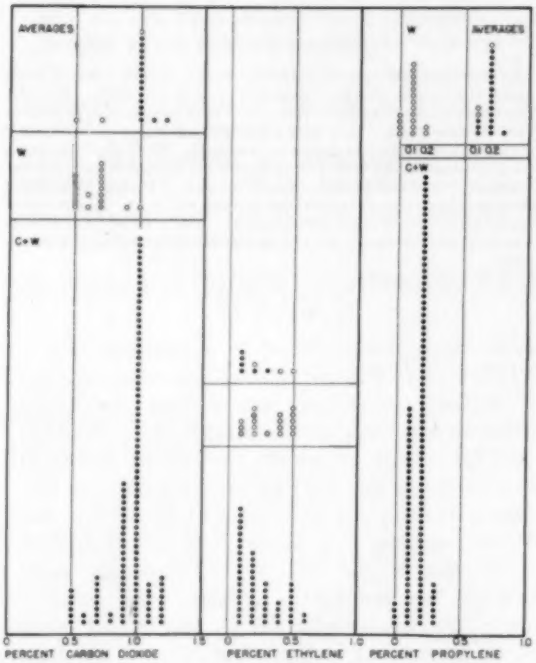

FIGURE 3.—*Frequency-distribution plots for carbon dioxide, ethylene, and propylene*

Carbon dioxide.—The greatest frequency appears at 1.0 percent. The arithmetical mean of the whole group is 0.94; but with the low W values excluded, the mean is 1.00. The most probable value, based on determinations within 0.1 percent of the value of greatest frequency, is 1.00±0.03 percent. Volumetric chemical analysis in an all-glass apparatus gave the value 1.00±0.02 percent.

Ethylene.—Was reported in nearly half of the analyses—51 out of 118 determinations—and by 10 of the 21 instrument-laboratory combinations. The greatest frequency appears at 0.1 percent, and the mean of all plotted values is 0.26 percent. All three of the W instruments reported this hydrocarbon; C instruments were not so unanimous, although 7 of the 18 indicated its presence. The uncertainty of opinion as to whether or not ethylene was present—43 percent for and 57 percent against—is interesting. There was no such uncertainty concerning propylene. In this connection, there was no positive correlation between low propylene and the presence of ethylene.

Propylene.—Although only about half of the analyses appeared to separate ethylene as a constituent of this sample, the identification of propylene was almost unanimous. Propylene was reported in 114 of 118 determinations, with the greatest frequency at 0.2, a mean of 0.2±0.04, and a mean of 0.2±0.03 for the laboratory averages. W instruments tend to the value 0.1 rather than 0.2. The total spread, 0 to 0.3 percent, and the high frequency at 0.2 percent attest the remarkable resolving power of the mass spectrometer in this instance. Special chemical analysis gave the result 0.19±0.04 as the total amount of C_3H_6 in this sample.

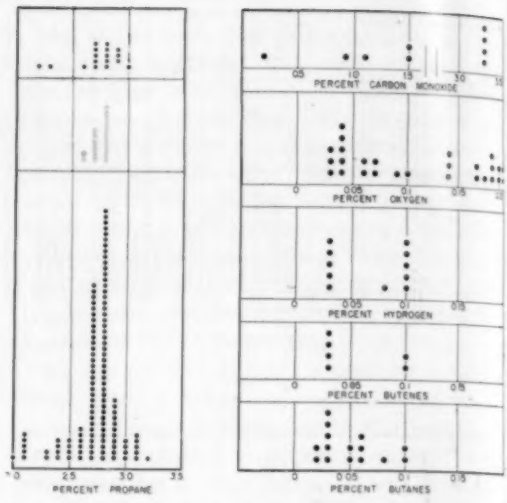

FIGURE 4.—*Frequency-distribution plots for propane and for various gases not in the sample.*

Propane.—These values spread over a range of only 1.2 percent, with a mean value of 2.7. Seventy-eight percent of the determination lie within 0.4 percent, with a mean value of 2.8±0.06. The greatest frequency is at 2.8 percent. The W values are well within the general group. The mean of the laboratory averages, excluding the two low values, is 2.8±0.1.

Carbon monoxide.—Only 9 of the 118 analyses "discovered" carbon monoxide. The distribution was random, and it is quite evident that N_2 and CO have been confused in some of the reported instances. There was no CO in this sample. NBS colorimetric indicating tubes were used to prove this fact. (Martin Shepherd, A preliminary report on the NBS colorimetric indicating gel for the rapid determination of small amounts of carbon monoxide, Anal. Chem. **19**, 77 (1947)).

Oxygen.—Reported in 27 out of 118 determinations (23 percent of the samples examined). The distribution was random. Smaller amounts may not have been significant, and larger amounts represented contamination with air, probably in transferring the sample to the spectrometer. The sample itself contained no oxygen.

Hydrogen.—Found in 11 of the 118 analyses, always in small amounts and with random distribution. There was no hydrogen in the sample. Its absence was established (within ±0.001 percent) by separation at the temperature of liquid hydrogen, using the apparatus and methods described in Bureau Research Paper RP75.

Butenes.—Only 6 of 118 determinations indicate the presence of butenes in small amounts (0.03 to 0.1 percent). It is very doubtful if butenes were present in this sample.

Butanes.—Reported in 15 of 118 determinations, in small amounts ranging from 0.02 to 0.1 percent, and with random distribution. It is possible that the sample may have contained about 0.05 percent of *n*+isobutane, but this is not certain. One laboratory analyzed a fraction of this sample condensed at low temperature, thus increasing the relative proportion of C_4 hydrocarbons if present. No C_4 component was identified.

The three Westinghouse instruments did not report CO, H_2, O_2, or C_4 hydrocarbons.

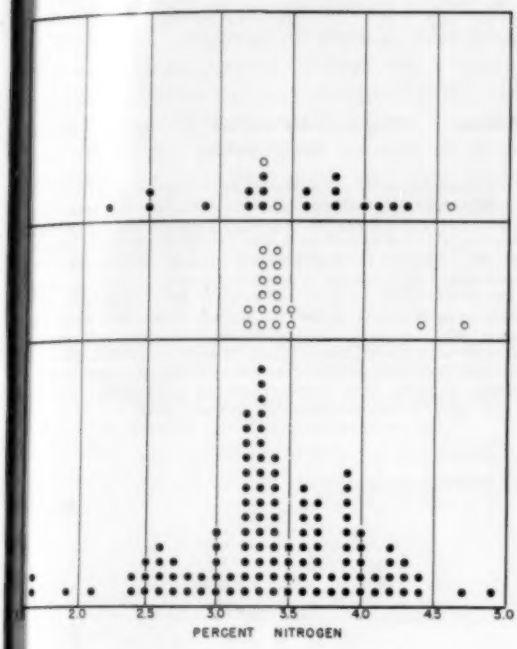

FIGURE 5.—*Frequency-distribution plot for nitrogen.*

Results for nitrogen are somewhat scattered over a range of 3.3 percent, with the greatest frequency at 3.4 percent. This casts some doubt upon the composition of the mixture with respect to this component. The mean of all determinations is 3.4, while the mean of values from 3.0 to 4.0 percent inclusive, representing 71 percent of the whole group, is 3.5±0.3. The laboratory averages ranged from 2.2 to 4.6 percent, with a mean of 3.5±0.5. Nitrogen was reported in 114 of the 118 determinations, but in four cases, nitrogen was identified as carbon monoxide. The W values are generally consistent with the best values to be derived. Volumetric chemical analysis in all-glass apparatus with direct measurement of residual inert gas gave the value 3.5±0.1 percent for this sample.

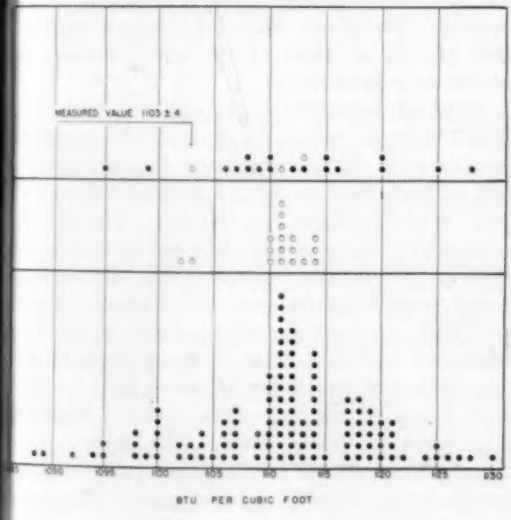

FIGURE 6.—*Frequency-distribution plot for the calculated heating value.*

The measured heating value of this sample was 1,103±4 Btu/ft³ (measurements were made with the Junker's calorimeter by J. H. Eiseman and R. Jessup of the National Bureau of Standards. This value was originally reported as 1,103 in RP1759, but the procedures for calculation as given in the new ASTM Tentative Method of Test for the Calorific Value of Gaseous Fuels by the Water-Flow Calorimeter, ASTM Designation D900–46T, shifts the value to 1,105 Btu/ft³). The values calculated from analyses by the mass spectrometer are generally higher than the measured value and extend over 42 Btu/ft³. The highest frequency appears at 1,111 Btu/ft³. The mean of all values is 1,111. The mean of values from 1,100 to 1,121, inclusive (about 85 percent of all determinations) is 1,112±4.4. The mean of the laboratory averages is 1,111±6. The W values are consistent with the more gregarious of the group. Values derived from the spectrometric analyses are thus higher than the measured value.

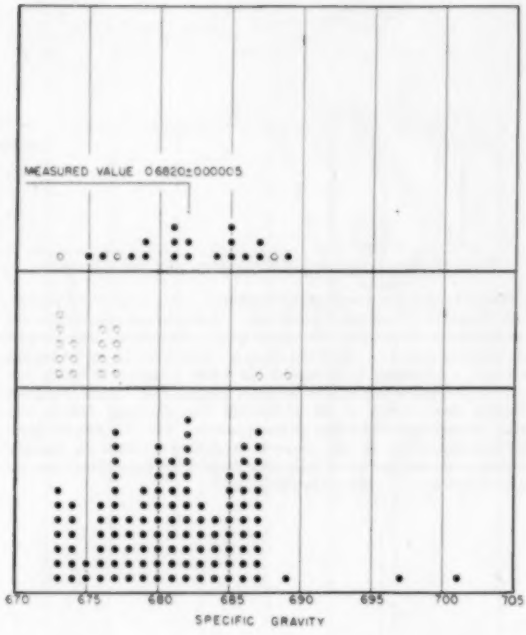

FIGURE 7.—*Frequency-distribution plot for the calculated specific gravity.*

The measured specific gravity of this sample was 0.6820±0.0005 (Made by Carroll Creitz. For details of this measurement, see NBS Miscellaneous Publication M177, "Tests of instruments for the determination, indication, and recording of the specific gravities of gases"). The specific gravity calculated from the analyses by the mass spectrometer spreads from 0.673 to 0.701, but if the three high values are excluded, this range is narrowed to a spread of 0.114. The results are evenly distributed with no apparent peak, and the group seems slightly lower than the true value. The mean of the group (three high values again eliminated) is 0.681±0.004. Thus, while the maximum deviation from the known value is 1.3 percent of this value, the average deviation is 0.6 percent. The W values are mostly lower than the known value. The mean of the laboratory averages is 0.682±0.004. The two values are in excellent agreement with the known value.

Before laying aside the frequency-distribution plots, a few high lights may be reviewed.

In dealing with about 77 percent of methane in a sample of natural gas, when relatively few determinations are made with one spectrometer selected at random, it is obviously not sensible to think in terms of tenths of a percent when the results obtained by the single spectrometer are to be compared with those of another selected at random. Such amounts may as well be reported to the nearest whole percent. Nearly the same can be said regarding amounts of ethane near 15 percent. However, propane in amounts around 3 percent can conscientiously be reported to the nearest tenth percent; and propylene present to the extent of 0.2 percent can probably be estimated to hundredths of a percent. But while 3 percent of propane can be reported to the nearest tenth percent, 3 percent of nitrogen cannot. Thus, a simple arithmetical convention for rounding out values, which is based only on the order of magnitude of the value, is not dependable.

The astonishing ability to detect and estimate properly 0.2 percent of propylene has been noted. But it is also evident that the mass spectrometer, with its great sensitivity for small amounts of many gases, is not infrequently capable of detecting gases actually not in the sample under examination. There are some who stoutly maintain that this is no fault of the spectrometers; but obviously it is no virtue.

Although some of the plots show a fairly wide distribution of values, in general, this horizontal displacement illustrating poor reproducibility is not so great here as for the corresponding chemical determinations previously reported.[7] By comparison, some of the chemical determinations were inconveniently various. The Westinghouse instruments did show some individuality—enough to cause speculation as to what would have happened had there been as many kinds of mass spectrometers and ways of using them as there were kinds of the volumetric chemical apparatus and ways of using them. The present need standardization of gas analysis by the mass spectrometer should be incorporated in a tentative standard before it is too late.

The plots have not shown the reproducibility achieved between different computers working

[7] See footnote 3.

with the same spectrogram, and between different spectrograms of this sample obtained on the same spectrometer. The reports disclose almost exact agreement in most cases between two computers picking, interpreting, and computing the same spectrogram. Disagreements did not exceed 0.1 percent for the components present in largest amounts. On the other hand, two spectrograms taken with the same spectrometer usually differed by amounts ranging from 0.1 to 0.8 percent. Disagreements of 0.4 or 0.5 were fairly frequent, and agreement to 0.1 was usually not achieved. Apparently checks or 0.2 to 0.3 percent represented the average best work. But it should be remembered that these variations represent the work of a single laboratory, and do not represent the variations among all of the laboratories.

Finally, the most probable composition as determined by all of the mass spectrometers can be set down:

Component	Percent (mole or volume)
Methane	77. 6
Ethane	14. 9?
Nitrogen	3. 4
Propylene	0. 2
Propane	2. 8
Carbon dioxide.	1. 0

These values correspond to the arithmetical means noted in the legends of the figures. They also represent the medians in every case but that of ethane, where the median is 14.7. Four of the six means were weighted after inspection of the frequency-distribution plot, which indicate how rogues may be weeded out. Unfortunately, this process usually involves some personal judgment and is questionable in direct proportion to the judgment invoked.

In the present instance, the argument is as follows: (1) In case of methane and ethane, one of the W instruments yielded a consistently high methane and a low ethane. This pattern strongly suggests a systematic error (for which an explanation is already at hand). Other values discarded were obviously away from the main block of determinations. Ethane remains in question, since the mode and median are 0.2 percent lower than the mean of all values or the weighted mean, while the weighted mean and the median agree for methane, and are only 0.1 percent lower than the mean of all values. (2) In the case of nitrogen, the mode is 0.1 percent lower than the weighted mean, unweighted mean, and median, all three of which are in agreement. (3) The mode, median, and unweighted mean for propylene are all in agreement, and no need for a weighted mean is evident. (4) The values from 2.6 to 2.9, inclusive, have been selected in the case of propane for the weighted mean, which is 0.1 percent higher than the mean for all values—a difference obtained by including obvious rogues around 2 percent in the mean for all determinations. Median and mode agree with the selected mean. (5) In weighing the values for carbon dioxide the mode was strongly influential, as was the knowledge derived from many chemical determinations of this component in the same sample. The chemical mode and mean, and the spectrometric mode, median, and weighted mean are all in agreement. The preponderance of low values in the W group suggests a systematic error.

IV. Calibrating Gases and Times of Calibration as Affecting Accuracy

The following observations should be qualified immediately by stating that the term "accuracy" is not used in its strictest sense, but is taken for the moment to mean agreement with the most probable values determined by all the spectrometers, which were noted in the foregoing section. It is known that inaccuracies occured when components known to be absent were reported. The real composition of the sample with respect to nitrogen (more strictly, inert), carbon dioxide, and propylene is closely known. The composition with respect to methane, ethane, and propane can be estimated rather well, but is not known to an order of magnitude better than the analytical resolution of the mass spectrometer. With these qualifications in mind, the facts concerning calibrating gases and time of calibration may be considered.

There were a number of sources of calibrating gases. In general, the hydrocarbons came from Phillips Petroleum Co., Ohio Chemical & Manufacturing Co., Matheson Chemical Co. and the Southern California Gas Co. The stated purity

of the various gases ranged from 98 to 99+ percent. Nitrogen and oxygen were derived from the commercial compressed gases, or the calibration was made with air. Carbon dioxide was obtained by the sublimation of the solid or from a cylinder of the liquid. Occasionally some of these gases were purified by distillation or prepared at home by the laboratory that used them for the calibrations. These cases were exceptional, and in only one instance was the entire list of calibrating gases given this especial treatment by a laboratory obviously not inclined to take chances. Since there was but this single case, it may not be worth noting that this laboratory reported results which in *all* cases checked the most probable or the known values to 0.1 percent or closer, a record not equaled elsewhere.

It might be expected that the apparent lack of strict standardization of calibrating gases would be a significant factor affecting accuracy, and indeed this may have been true. But aside from the case just cited, there is no direct evidence of this. There is no correlation between the source of calibrating gas and the amount or direction of the deviation from probable or known values. The correlation in the exceptional case may have as its real basis, not the purity of calibrating substances, but the fact that an operator who insisted upon very unusual care in the preparation of pure calibrating gases would be more than likely to exercise very unusual care in the subsequent analyses.

It might further be expected that more reliance could be placed upon analyses that were computed with calibrating patterns obtained at the same time as the pattern of the unknown. This assumption remains reasonable, even though the reports again failed to show a definite correlation between accuracy and the relative time of calibration and analysis. In a majority of the cases, the calibration patterns were obtained within a week of the patterns for the unknown sample. In many cases, calibration and analysis were made within 24 hours of one another. But there were enough calibrations made 1, 2, or even 3 months preceding the analysis to show any tendency toward loss of accuracy from this cause—and no such tendency appeared in the data submitted. The conclusion is that, for the present, other factors are more important. But this conclusion does not justify failure to calibrate as often as one desires to know what really goes on. Certainly too little is known about these matters, and until more information is available and the proper requirements are finally developed, it seems reasonable to proceed with greater care than may be necessary.

V. Conclusions

The particular needs are a better reproducibility for methane, ethane, and nitrogen, and less enthusiasm in the matter of reporting components actually not present. The tendency toward too-high calculated heating values suggests an imbalance between the lighter and heavier hydrocarbons. But in general the reproducibility attained was better than that of the chemical methods. One reason for this would appear to be a fair degree of standardization which exists because the method is new and has not yet been subject to great variation of apparatus and procedure. Somehow, the advantage of this standardization should be captured. An ASTM standard is planned as one means of doing this.

Jean Doyle and Marthada Vaughn Kilday checked the calculations of heating value and specific gravity, and this assistance is gratefully acknowledged. Churchill Eisenhart and Celia Martin of the Bureau's Statistical Engineering Section corrected errors in the frequency-distribution plots.

Washington, March 12, 1947.

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Infrared Emission Spectra of Krypton and Argon

By Curtis J. Humphreys and Earle K. Plyler

The analysis of the spectra of the noble atmospheric gases, utilizing descriptive data covering the photographically accessible region, has long indicated the possibility of a considerable extension of most of these spectra into the infrared region beyond 1.3 microns. Observations of the spectra of krypton and argon, in the region between 1 and 2 microns, have been made with a Perkin-Elmer spectrometer, fitted with a flint-glass prism cut to an angle of 55 degrees. The sources were Geissler tubes, used in previously reported work.

More than 15 new lines of krypton have been observed. Part of these are blends of unresolved pairs or groups. The emission maxima have been determined in favorable cases to a precision of two wave numbers, roughly equivalent to one-tenth of the smallest scale division on the wavelength drum. All observed lines have been classified, the most intense being represented by combinations of the type $2p$–$3d$, according to Paschen's notation. Two new levels from the configuration s^2p^5f have been found. The remaining unobserved combinations of the type $1s$–$2p$, occurring in this region, are, with one exception, too weak to be observed. The argon infrared spectrum was observed by Paschen. More of its predicted combinations are in the photographic region than in the case of krypton. A few lines near 1.4 microns have been observed.

I. Introduction

The spectra originating in the neutral atoms of the noble atmospheric gases, neon, argon, krypton, and xenon, are among the most thoroughly studied of all line spectra observed and described to date. Examination of published data reveals very few lines of appreciable intensity that have not been fitted into a scheme of energy levels in accordance with the theory now universally accepted.

The first detailed and relatively complete analysis of any of the first spectra of the noble gases was that of neon, published by Paschen [1] [1] in 1919. Paschen used a special notation to represent the spectral terms of neon. His system has been generally followed by other investigators reporting on the first spectra of the remaining noble gases, and is used in this paper.

The first spectrum of argon was classified by Meissner and reported in a series of papers beginning in 1926 [2]. In 1929 Gremmer [3] published the classification of the more prominent lines. He also extended the analysis of neon and argon in the photographically accessible infrared [4]. In 1929 also, Meggers, de Bruin, and Humphreys [5] published a detailed analysis of the first spectrum of krypton. Improved observations making available double the number of lines permitted a further extension of this classification in 1931 [6], with some minor revisions. A new paper by Gremmer [7] showed how all discrepancies between his analysis and that of Meggers, de Bruin, and Humphreys could be reconciled. Additional lines in the red and infrared were reported by Rasmussen [8].

The first spectrum of xenon was classified by Meggers, de Bruin, and Humphreys [9], with a subsequent revision and extension by Meggers and Humphreys [10]. Gremmer [11] also published an analysis in essential agreement with that of the authors just named. Rasmussen [8]

[1] Figures in brackets indicate the literature references at the end of this paper.

extended the classification and contributed additional infrared data.

The above résumé of work on the first spectra of the noble gases is by no means complete. It includes references only to papers in which the analyses were brought to essentially their present form. The publications cited, however, give the complete history of the subject back to the discovery of these elements.

As soon as the energy-level systems for the noble gas atoms were fairly well established, it became evident that many relatively intense lines should occur in the infrared. The discovery of improved sensitizers for photographic plates has permitted a number of extensions of these spectra in the direction of greater wavelengths. Meggers and Humphreys published a paper on the infrared spectra of neon, argon, and krypton in 1933 [12]. Photographic observations as far as 12,000 A were reported. The paper also listed radiometric observations previously published by Paschen [13] on argon, and by Hardy [14] on neon. Complete term tables were given, incorporating the extensions permitted by the new data. These tables should be consulted in order to understand the discussion of the location of infrared lines as given in succeeding paragraphs. A later publication by Meggers [15] gives wavelengths and classifications of helium, neon, argon, krypton, and xenon lines as far as 13,000 A. These observations were made with Z-type Eastman plates and represent the present limit of photographic observations, utilizing silver halide emulsions incorporating photosensitizing dyes.

II. Location of Infrared Emission Lines

In conformity with generally observed characteristics of the spectra of homologous elements, there is a shift of analogous term combinations toward longer wavelengths as one goes from elements of lower to those of higher atomic number in the array of noble gases. In the first spectrum of neon most of the $1s$–$2p$ combinations are in the yellow, orange, and red regions and give the discharge its characteristic color. The $2p$–$3d$ combinations are in the photographically accessible infrared region, and appear with great intensity on plates treated with special sensitizers. The only combinations, in neon I, out of the range of photography in the infrared, are those of the $3d$ levels with the levels originating in the lowest f-electron configuration, and possibly as many as eight combinations of the type $2p$–$2s$.

In argon I, fewer $1s$–$2p$ combinations are in the visible region than in neon I, but all of them can be photographed. About half of the $2p$–$3d$ combinations are in the photographic range. The others are to be expected between 1.3 and 3 μ. The d–f combinations involving lowest possible total quantum numbers are almost all just beyond the photographic region. Combinations of the type $2p$–$2s$ are in approximately the same region as $2p$–$3d$, and all the $2s$ levels have been established by photographic observations.

The structure of krypton closely resembles that of argon with a somewhat greater displacement of analogous combinations toward greater wavelengths. Five of the $1s$–$2p$ combinations are beyond the range of photography, and extend as far as 2 μ. The $2p$–$3d$ combinations are predicted in the range between 1 and 10 μ, a few being of still greater wavelength. A number of these transitions have been observed photographically, namely, in instances where the p-level series converges to the lower, and the d-level to the higher ion limit. The d–f combinations of first members of these series are, with a few exceptions, of a wavelength too great for photography. The second members of the s-series are of about the same magnitude as the first members of the d-series. This brings the $2p$–$2s$ combinations within the same range as those of the type $2p$–$3d$.

The predicted distribution of xenon lines in the infrared is considerably different from that of the other noble gases. Five $1s$–$2p$ combinations have not been observed. They are all too far out in the infrared for the radiation to be transmitted by the glass enclosures of the sources used in this work. They are also combinations between levels converging to different limits and not expected to be very intense. The $2p$ and $3d$ levels are of about the same magnitude, placing the combinations for the most part beyond the range of glass transmission. The interlimit transitions of the $2p$–$3d$ type fall mostly in the photographic range. This results from the very large difference between the ion limits amounting to 10,540 cm^{-1}. The d–f combinations fall in the photographic range. Only one of the $2s$ levels is known.

It may be concluded that, of these spectra, krypton I, and argon I, may be expected to have

considerable number of intense combinations between 1μ and 2μ. Almost all intense neon lines may be photographed, whereas xenon has a very sparsely populated region between the photographic limit and about 5μ. These considerations indicate that krypton and argon are the most promising of the noble gases for study in the region just beyond the limits of photography, but in which the glass enclosures of available sources are transparent.

III. Observations

The sources used in the earlier observations at the National Bureau of Standards were, for the most part, Geissler tubes, made by Robert Götze, in Leipzig, and of special construction permitting end-on illumination of the spectrometer slit. Several of these tubes were still in excellent condition, and were made available for these observations by the kindness of W. F. Meggers, of the Bureau's Spectroscopy Section.

A Perkin-Elmer model 12A spectrometer, equipped with a General Motors amplifier and Brown recorder, was used as the dispersing, detecting, and recording system. Only slight modifications of this system were needed. The housing covering the projecting system was lifted, and the plane mirror rotated by a sufficient amount to permit forming on the entrance slit an image of the emission source, which was mounted beside the globar housing. The first recordings were made with the rock-salt prism in place. These served to establish the existence of the emission spectrum in the region between 1.3 and something over 2μ. This, however, is near to the region of minimum dispersion for rocksalt, so that the conditions for wavelength measurement are unfavorable. Subsequently, a flint-glass prism cut to an angle of 55 degrees was mounted in the spectrometer. This angle was calculated to permit operating the instrument within the range of available wavelength dial settings without changing the setting of the Littrow mirror. By a proper selection of the prism angle, it is possible to interchange prisms of different materials without any readjustment of the other components, and to maintain the calibration for each prism.

Wavelength calibration was obtained by use of an H-4 mercury lamp. This is a source of high intensity and is steady in operation. The arc stream appears as a thin line when the source is warmed up, permitting a large concentration of energy in the slit opening. With this source it was possible to work with slit openings of 15 μ, and in some instances down to 12 μ. The mercury spectrum in the infrared is well known from the observations of McAlister [16], who used a glass multiprism spectrometer of high resolution, obtaining wave numbers that agreed remarkably well with those calculated from the known level scheme. The dial settings corresponding with the emission peaks of the mercury lines were determined from the averages of six recordings, and can be established to within one-tenth of a scale division. The mercury spectrum gives a good distribution of lines up to nearly 2 μ. The weakness of this array in a prismatic spectrum is that the four strongest lines at the longer wavelength end, namely, 1.6919, 1.6935, 1.7073, and 1.7108 μ, appear as two emission peaks, each consisting of an unresolved pair. The latter pair has a separation of 12 cm^{-1} in wave number and is just beyond the practical limit of resolution at this setting. The averages of the wave numbers of the respective pairs were adopted as the values for the observed peaks. It is expected that more satisfactory standards for the 2-μ region can be found when more intense sources are available. Possibilities are the helium line at 2.058 μ and the hydrogen line at 1.875 μ, the latter being the first line of the Paschen series. The wave numbers of the mercury lines were plotted against observed dial settings to give the calibration curve.

The noble gas sources were operated in the usual manner by connecting the tubes directly to the secondary of a sign transformer, rated at 12,000 v, 200 va. A variable-voltage transformer was placed in the primary to control the input voltage so as to prevent overloading. The energy output of these tubes was extremely small as compared with the mercury source. It was necessary in general to operate the amplifier gain setting as high as possible. This required unusually good operating conditions in the room because very slight temperature changes caused a large amount of zero drift. The slit settings were kept as small as possible, consistent with reasonable deflections, but in general it was necessary to operate in the range of slit-width settings between 60 and 120 μ. Repeated runs were made with different amplifier gains and different slit widths, chosen to give the best record of characteristic features. Thus the

most intense lines could be observed with narrower slits and lower amplifier gains, whereas it was necessary to increase both to the practical limit in order to obtain the faintest lines. It was encouraging to find, however, that the sharpest maxima could be determined with a precision of about one-tenth of a scale division from repeated records. The less well-defined maxima are probably fixed with a precision about half as great. At 6,000 cm^{-1}, a scale division corresponds to about 15 wave numbers, when the glass prism is in place.

The portions of the red and infrared spectra of krypton and argon falling within the range of photographic observation have been reobserved by the methods reported in this paper. The wavelengths of the lines so observed were found to conform with the system of mercury standards and with the noble gas lines of lesser wavelength. Inasmuch as these lines have already been observed with a precision that could not be matched with the radiometric technic used in this work, they are not listed in this paper except where classified on the basis of new observations.

IV. Discussion of Results

The results obtained for krypton, together with their interpretation, are shown in table 1. Here are shown observed wave numbers and corresponding wavelengths, estimated intensities on a scale 1 to 10, calculated wave numbers, and interpretation as combinations of levels. The first two lines entered in the table were observed, but, inasmuch as the calibration curve obtained from mercury lines cannot be extrapolated with reasonable accuracy beyond about 1.7 μ, only the wave numbers, computed from known level values, are listed.

The surprising feature of this spectrum is the failure of the previously unobserved $1s$–$2p$ combination to appear with appreciable intensity. The line with adopted wave number 5,322 classified $1s_5$–$2p_{10}$ is the only one of this group appearing with sufficient intensity to be observed by the Bureau's present equipment.

The most intense krypton lines observed are combinations of the type, $2p$–$3d$. These can be classified both on the basis of computed wave numbers and the intensities of the higher members of the respective series, all of which are observed photographically. The fact that the combinations $2p_8$–$3d_4$ and $2p_9$–$3d'_4$ show the highest intensities among this group is in accordance with expectations. The line observed at 5,930 cm^{-1} is much stronger than any of the others. As noted in the table, it is possible that five different lines may contribute to this maximum. Considering the slit widths that were required, it is probable that the limit of resolution when using the noble gas sources was not better than about 25 cm^{-1}, so that these ambiguities cannot be avoided until the technic can be improved.

TABLE 1.—*List of* Kr I *lines*

Intensity	$\lambda_{obs.}$	$\nu_{obs.}$	Term combination	$\nu_{calc.}$
	Microns	cm^{-1}		cm^{-1}
1	----------	----------	$1s_2$–$2p_{10}$	5,322
5	----------	----------	$2p_9$–$3d_4$	5,503
1	1.7820	5,610	$2p_{10}$–$3d_4$	5,603
1	1.7347	5,763	$2p_7$–$3s''_1$	5,756
10	1.6859	5,930	$2p_9$–$3d_1$	5,919
			$2p_7$–$3d_4$	5,932
			$2p_{10}$–$3d_3$	5,917
			$2p_7$–$3d'_1$	5,903
			$2p_8$–$3d'_1$	5,956
1	1.5823	6,318	$3d_2$–4X	6,319
			$3d_2$–4Z	6,320
4	1.5326	6,523	$2p_{10}$–$3d_3$	6,519
			$2p_8$–$3d_2$	6,522
3	1.4747	6,779	$2p_9$–$3d'_1$	6,785
			$2p_8$–$3d_1$	6,772
			$2p_8$–$3s_1$	6,771
3	1.4424	6,931	$2p_7$–$2p_4$	6,930
			$2p_7$–$2p_2$	6,942
			$3d'_1$–4X	6,942
2	1.3926	7,179	$3d''_1$–4W	7,180
6	1.3631	7,334	$2p_9$–$3d_2$	7,358
			$2p_8$–$2p_3$	7,333
2	1.3203	7,572	$2p_8$–$2p_1$	7,567
2	1.2883	7,760	$3d_4$–4U	7762.1
1	[a]1.220454	8191.43	$3d'_4$–4U	8191.43
	[a]1.211781	8250.06	$3d'_4$–4W	8250.06

[a] Wave lengths given by W. F. Meggers.

There are a number of combinations of the type $2p$–$2s$. However, there is still no evidence for the missing $2s_3$ term. As it has not been found from photographic data, only a combination involving $2p_3$ or $2p_4$ could reveal it.

The remaining lines are classified as combinations of f-type levels. Two of these designated 4U and 4W, are new. It is interesting to note that they explain two previously unclassified lines given by Meggers, at wave numbers 8250.06 and 8191.43. The level values, in accordance with the latest revision of the krypton term table

[12], and respective inner quantum numbers are as follows:

4U, 6926.04, $j=4$

4W, 6867.41, $j=3$.

The experimental evidence for these new levels is the appearance of two constant differences, the first, between the lines 8191.43 and 7,760 cm^{-1}, equal to the difference between $3d'_4$ and $3d_4$, and the second, between the lines 8,250.06 and 7,179 cm^{-1}, equal to the difference between $3d'_4$ and $3d''_1$. Each of these differences established a new level. Additional evidence that removes any doubt as to the reality of these levels, is that extrapolation of the hitherto incomplete series, designated U and W, back to their respective first members, gives values practically identical with those experimentally determined for the two new levels. It becomes apparent therefore, that these levels are the first members of the U and W series, and the reason for the choice of designation is obvious. These *f*-type series are nearly hydrogenic and can be readily extrapolated by means of a Rydberg table [17].

Very few new data were obtained for the argon spectrum, since most of it is in the photographically accessible region. Two of the lines observed by Paschen, 7402.9 and 7287.3 cm^{-1}, are those of greatest wavelength to appear with appreciable intensity. An emission peak at 7,477 cm^{-1} is probably $2p_6$–$3d'_1$, or $2p_2$–$2s_2$ or a blend of these.

V. Conclusion

The infrared measurements reported in this paper are to be regarded as preliminary. The investigation was intended to demonstrate the feasibility of exciting these spectra with sufficient intensity for observation, and of operating with available apparatus and methods. Work is in progress on the design and construction of new apparatus for study of line emission spectra in the infrared. The principal unit is to be a grating spectrometer equipped with a grating ruled to concentrate the radiant energy in a selected region. Several such gratings will be available. A second improvement that must be made is the utilization of sources permitting very much greater concentration of incident radiation at the entrance slit of the spectrometer.

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Dipole Moments and Resonance of Some Benzein Indicators and Related Compounds

By Arthur A. Maryott and S. F. Acree

An apparatus for the measurement of dielectric constants of liquids by the heterodyne method and, in particular, for the determination of dipole moments is described. Dipole moments ($\times 10^{18}$ electrostatic unit (esu)) are reported for, 4-hydroxybenzophenone (3.96), 4,4′-dihydroxybenzophenone (4.49), 4-hydroxy-2-methyl-5-isopropylbenzophenone (3.59), fuchsone (5.83), benzaurin (6.85), aurin (7.96), *o*-cresolbenzein (6.70), thymolbenzein (6.67) and α-naphtholbenzein (6.07) using dioxane as solvent. The last six compounds contain the quinoidal structure and have unusually large moments. The values are nearly double those found for the derivatives of benzophenone that have corresponding polar groups. The influence of resonance involving highly dipolar excited structures in determining the actual state of these molecules is discussed.

I. Introduction

Development in recent years of the concept of uantum-mechanical resonance has been of value interpreting the physical and chemical behavior many types of organic molecules [1, 2].[1] The rrelation between spectral absorption in the sible region by organic dyes and indicators and sonance has been emphasized by Bury [3]. A mber of investigators, but particularly Brooker d coworkers [4], have had notable success in terpreting in terms of resonance certain characteristics of absorption in colored organic mpounds.

Dipole moments of dyes and indicators are of terest in connection with the type of resonance hich includes highly dipolar structures, as illustated in figure 2 by structures II and III. The tual structure and charge distribution depend pon the relative contributions from the various ructures involved in the resonance. When ghly dipolar structures contribute significantly, e observed dipole moment differs from and is nerally greater than that to be expected from a nsideration of the classical structure alone, and e magnitude of this difference indicates the portance of these dipolar structures in the sonance.

The dipole moments of α-naphtholbenzein and thymolbenzein previously reported [5] were considerably larger than one would expect from a consideration of the classical structures alone. In the work now reported the measurements include other indicators of the benzein series and also some related hydroxybenzophenones that have corresponding polar groups. Structurally, the benzeins, or hydroxyfuchsones, differ from the familiar phenolphthalein and phenolsulfonphthalein series of indicators only in not having the carboxyl or sulfonic acid group. The compounds measured include 4-hydroxybenzophenone, 4,4′-dihydroxybenzophenone, 4-hydroxy-2-methyl-5-isopropylbenzophenone (thymolphenylketone), diphenylquinomethane (fuchsone), 4′-hydroxyfuchsone (benzaurin), 4′,4″-dihydroxyfuchsone (aurin) 4′-hydroxy-3,3′-dimethylfuchsone (*o*-cresolbenzein), 4′-hydroxy-3,3′-diisopropyl-6, 6′dimethylfuchsone (thymolbenzein), and α-naphtholbenzein. For brevity the names in parentheses will be used hereafter. The measurements were made with dioxane and, in several cases where solubility permitted, benzene as solvents. The moments found for fuchsone and the various hydroxyfuchsones are much larger than those of benzophenone and the corresponding hydroxy derivatives and indicate that dipolar resonance structures make a significant contribution to the actual state of these molecules.

[1] Figures in brackets indicate the literature references at the end of this paper.

II. Materials

Thiophene-free benzene was refluxed and distilled over sodium just before use. Technical dioxane was purified by the method recommended by Weissberger [6] and then distilled over sodium immediately before use. 4-Hydroxybenzophenone and 4,4′-dihydroxybenzophenone were supplied by the Dow Chemical Co. The 4-hydroxybenzophenone was recrystallized from benzene, then from an ethanol-water mixture, and again from benzene. The melting point, 131° to 132° C did not change after the first recrystallization from benzene. The 4,4′-dihydroxybenzophenone was first washed with boiling benzene to extract the more soluble impurities and then recrystallized three times from an ethanol-water mixture. The melting point was 213° to 214° C. Purified samples of fuchsone and aurin were furnished by W. C. Bainbridge of H. Kohnstamm & Co., Inc.[2] Purified samples of thymolbenzein and thymolphenylketone were obtained from Cornell University.[3] α-Naphtholbenzein from Eastman Kodak Co. was twice recrystallized from glacial acetic acid. Additional recrystallization gave no further change in the molar absorption index determined with a Coleman model 10S spectrophotometer. Benzaurin was prepared by condensation of phenol with benzotrichloride [7]. The crude material was purified by two recrystallizations from glacial acetic acid. The melting point was 238° to 240° C. All materials were dried to constant weight in a vacuum oven at about 110° C. Carbon and hydrogen microanalyses were made by K. D. Fleischer on the following compounds:

Name	Found		Calculated	
	C	H	C	H
Thymolphenylketone	80. 4	7. 1	80. 28	7. 14
Fuchsone	88. 1	5. 5	88. 34	5. 47
Aurin	78. 4	4. 8	78. 59	4. 86
Thymolbenzein	83. 7	7. 8	83. 80	7. 83
αNaphtholbenzein	86. 1	4. 9	86. 61	4. 86

[2] The authors express their appreciation to W. C. Bainbridge and coworkers for specially preparing and purifying these materials.

[3] These compounds were made available through the kindness of J. R. Johnson.

III. Apparatus

Measurements of capacitance were made by heterodyne beat method [8]. A photograph of th assembled equipment is shown in figure 1. A RCA-type 154 beat-frequency oscillator with th following modification was used as the radi frequency source. The 450-μμf mica condenser i the tuned circuit of the variable oscillator wa replaced by an equivalent capacitance consistin of a General Radio Co. type 722–N direct-readin precision condenser in parallel with the cell used fo measuring dielectric constants. The fixed oscilla tor, which had a fundamental frequency o approximately 350 kc, was left intact. The inpu voltage was stabilized by means of a voltag stabilizer. The output of the oscillators wa coupled resistively with a 1,000-cycle tuning for electrically excited. The resulting beat note wa then audible in a set of earphones used as th indicating device.

The precision condenser was equipped with micrometer worm-gear drive to supplement th regular worm drive in order to increase th precision of setting. The scale of the micromete contained 50 divisions with each, corresponding t a capacitance of about 0.004 μμf. The condens was calibrated by a step method using a capac tance of approximately 3 μμf. A plot of th calibration correction with respect to scale readin showed a very definite periodicity correspondin with each complete revolution of the mai worm drive.

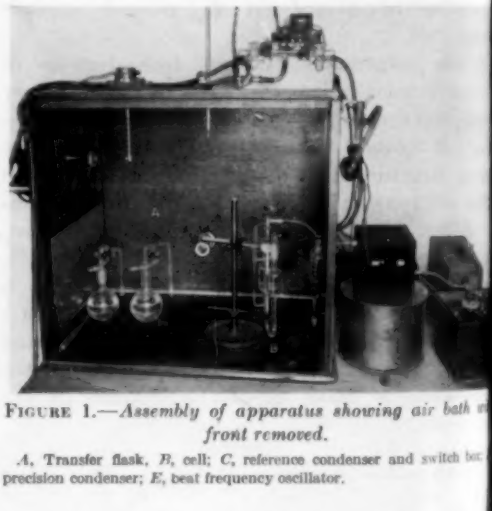


FIGURE 1.—*Assembly of apparatus showing air bath w front removed.*

A, Transfer flask, *B*, cell; *C*, reference condenser and switch box precision condenser; *E*, beat frequency oscillator.

The cell was made of Pyrex glass, in which the two concentric electrodes were formed by deposition of a heavy silver mirror on the appropriate glass surfaces. Contacts between electrodes and leads were by thin platinum wires sealed through the glass walls. The cell was made in two sections which fitted together by means of a ground-glass joint. After deposition of the silver films, this joint was cemented rigidly in place. The inner section contained the ungrounded electrode with the lead, a rigidly mounted, small brass rod, passing up through the center. Contact between the platinum wire and rod was made with mercury held in place with cellulose nitrate cement. This lead was thoroughly shielded with a grounded brass tube. The outer section contained, in addition to the grounded electrode and lead, two enlarged bulbs of about 100-ml capacity each. These bulbs served as a reservoir to accommodate excess solution required in the procedure for making up solutions of varying concentrations to be described. The minimum volume of liquid needed to give constant capacitance was about 20 ml. The interelectrode air capacitance was approximately 40 $\mu\mu f$. Calibration of the cell was made with freshly purified benzene using the data of Hartshorn and Oliver [9] for the dielectric constant.

As the oscillator frequency drifts with time, some method is needed to eliminate the effect of this shift in frequency on the measured cell capacitance. Consequently, a reference air condenser of approximately the same capacitance as that of the cell when filled with solvent was arranged so that it could be substituted for the cell by means of a low-capacitance switch. The time required for settings was only a fraction of a minute, so the difference in capacitance between the cell and reference air condenser could be determined independently of any gradual drift in frequency of the oscillator.

An air bath was used to control the temperature of the cell at 32° ± 0.04° C. The temperature and relative humidity of the room containing the complete assembly were controlled at 25° ± 1° C and 50 ± 3 percent, respectively. The sensitivity and stability of the apparatus were such that a change of 0.0001 in dielectric constant could be detected.

IV. Experimental Procedure

One of the chief sources of error in the determination of dipole moments from measurements on highly dilute solutions arises from contamination of the solvent and solutions, particularly by moisture from the air, during handling. Consequently, the design of the cell and the procedure for making up the solutions of varying concentrations were such as to minimize handling and exposure to the air. The solvent was distilled directly into a specially designed transfer flask. Then, by means of dried compressed air, part of this solvent was transferred to the cell and part used in making up a stock solution of solute. Solutions of varying concentrations were made up directly in the cell by successive additions of this stock solution from a weight burette. After each addition, mixing was accomplished by forcing, with dried compressed air, the solution into one of the bulbs and then into the other. When measurements of capacitance were completed on the final solution, a portion of this solution was transferred to a picnometer for determination of density. The density of the same batch of pure solvent was also determined.

V. Calculations and Data

Calculation of the molar polarization at infinite dilution, $P_{2\infty}$ was made by using the following equation given by Hedestrand [10], in which the subscripts 1, 2, and 12 refer respectively to solvent, solute, and solution.

$$P_{2\infty}=\frac{3P_1}{(\epsilon_1-1)(\epsilon_1+2)}\frac{\Delta\epsilon}{f_2}-\frac{P_1}{d_1}\frac{\Delta d}{f_2}+P_1\frac{M_2}{M_1}, \quad (1)$$

where

ϵ = dielectric constant

$\Delta\epsilon=\epsilon_{12}-\epsilon_1$

f = mole fraction

d = density

$\Delta d=d_{12}-d_1$

M = molecular weight

$P_1=\frac{\epsilon_1-1}{\epsilon_1+2}\frac{M_1}{d_1}$ = molar polarization of solvent.

The dipole moment, μ, was calculated from

$$\mu = 0.1281[(P_{2\infty} - P_E)T]^{1/2} \times 10^{-18} \; esu, \qquad (2)$$

where T is the temperature in degrees Kelvin, and P_E is the electronic polarization obtained by summation of the atomic refractivities listed in Landolt-Börnstein Tabellen, fifth edition.

The experimental and calculated data are given in table 1. A plot of $\Delta\epsilon$ vs f_2 was linear in each case. The slope of this line given in the third column opposite zero concentration was used in the evaluation of $P_{2\infty}$[4]. The separate values of $\Delta\epsilon/f_2$ for each concentration are also given for comparison. The average of these separate values agrees closely with the slope of the linear plot in all cases and shows that the lines pass through the origin, as should be the case. The three values of $\Delta d/f_2$ in parenthesis are based upon the estimated partial molar volumes of these compounds and the assumption of ideal mixing. In these cases the concentrations were rather low for the experimental determinations to be conveniently made. Because of the relatively small magnitude of the term in eq 1 containing $\Delta d/f_2$, the uncertainty in these estimates will have a practically negligible effect upon the dipole moments calculated. As an example, a 20-percent error in this estimate would alter the moment calculated for aurin by only 0.1 percent. The dielectric constant of dioxane by comparison with that of benzene was found to be 2.210. The value for benzene at 32° C was taken as 2.260 [9].

[4] The method of obtaining $P_{2\infty}$ and μ by using the Hedestrand equation, which is the limiting form of the Debye equation as the concentration approaches zero, has certain advantages particularly for measurements on highly dilute solutions. The amount of calculation is minimized and frequently more reliable values are obtained than with the procedure usually employed, which involves a separate calculation of P_2 at each concentration and then extrapolation to infinite dilution. As has been pointed out by Kumler [11], this latter method unduly weights one experimental point, namely, the dielectric constant of the solvent itself, so that a small error in its value may produce a relatively larger error in $P_{2\infty}$ and μ. A linear variation of $\Delta\epsilon$ with f_2 is characteristic of dilute solutions provided, of course, the solute is not appreciably associated. A straight line not passing through the origin suggests an error in the dielectric constant of the pure solvent. Errors attributable to this source have rather frequently led to incorrect values of the dipole moments when the usual method of calculation has been employed [11].

Similar considerations apply equally well to determinations of density, except that errors in density are often much less critical. As densities vary practically linearly with concentration for dilute solutions, it is generally unnecessary to determine densities of more than one or two of the more concentrated solutions.

TABLE 1.—*Experimental and calculated data from which dipole moment, μ, is obtained*

$f_2 \times 10^3$	$\Delta\epsilon$	$\Delta\epsilon/f_2$	$\Delta d/f_2$	$P_{2\infty}$	P_E	μ
4-HYDROXYBENZOPHENONE IN DIOXANE						
0.000	.....	22.2	0.389	371	57	esu 3.96×10^{-18}
4.442	0.0992	22.3	.....	.....	.....	
5.202	.1157	22.2	.....	.....	.....	
7.420	.1647	22.2	.....	.....	.....	
8.960	.1990	22.2	.....	.....	.....	
4,4'-DIHYDROXYBENZOPHENONE IN DIOXANE						
0.000	.....	28.5	0.597	461	58	4.49
2.404	0.0714	29.7	.....	.....	.....	
3.554	.1001	28.2	.....	.....	.....	
6.526	.1877	28.8	.....	.....	.....	
9.522	.2718	28.5	.....	.....	.....	
THYMOLPHENYLKETONE IN DIOXANE						
0.000	.....	18.3	0.22	333	75	3.59
1.066	0.0193	18.1	.....	.....	.....	
2.184	.0397	18.2	.....	.....	.....	
2.915	.0533	18.2	.....	.....	.....	
3.593	.0656	18.3	.....	.....	.....	
THYMOLPHENYLKETONE IN BENZENE						
0.0000	.....	15.5	0.66	298	75	3.34
.3834	0.0059	15.4	.....	.....	.....	
.8123	.0125	15.4	.....	.....	.....	
1.037	.0163	15.7	.....	.....	.....	
FUCHSONE IN DIOXANE						
0.0000	.....	47.5	0.36	758	79	5.81
.3105	0.0153	49.2	.....	.....	.....	
.7112	.0344	48.3	.....	.....	.....	
1.015	.0489	48.2	.....	.....	.....	
1.282	.0611	47.6	.....	.....	.....	
FUCHSONE IN BENZENE						
0.0000	.....	46.1	0.75	752	79	5.80
.6203	0.0288	46.4	.....	.....	.....	
1.264	.0582	46.0	.....	.....	.....	
1.790	.0824	46.1	.....	.....	.....	
2.255	.1037	46.0	.....	.....	.....	
BENZAURIN IN DIOXANE						
0.0000	.....	65.6	0.56	1,022	81	6.82
.1696	0.0111	65.4	.....	.....	.....	
.3515	.0231	65.7	.....	.....	.....	
.5423	.0357	65.8	.....	.....	.....	
.6878	.0450	65.5	.....	.....	.....	

TABLE 1.—*Experimental and calculated data from which dipole moment, μ, is obtained*—Continued

$f_2 \times 10$	$\Delta\epsilon$	$\Delta\epsilon/f_2$	$\Delta d/f_2$	$P_{2\infty}$	P_E	μ
AURIN IN DIOXANE						
0.0000	------	88.0	[a] (0.7)	1,352	82	7.96
.0623	0.0054	86.8	------	------	---	
.0706	.0063	89.2	------	------	---	
.1059	.0092	86.9	------	------	---	
.1174	.0103	87.7	------	------	---	
.1340	.0120	89.5	------	------	---	
.1567	.0136	86.8	------	------	---	
o-CRESOLBENZEIN IN DIOXANE						
0.0000	------	62.5	(0.5)	985	90	6.70
.0935	0.0058	62.0	------	------	---	
.1028	.0065	63.2	------	------	---	
.1594	.0098	61.5	------	------	---	
.2043	.0130	63.5	------	------	---	
.2139	.0132	61.7	------	------	---	
.2714	.0171	63.0	------	------	---	
THYMOLBENZEIN IN DIOXANE						
0.0000	------	62.2	0.32	1,010	118	6.67
.2038	0.0123	60.4	------	------	---	
.3468	.0212	61.2	------	------	---	
.4606	.0283	61.4	------	------	---	
.5513	.0339	61.5	------	------	---	
α-NAPHTHOLBENZEIN IN DIOXANE						
0.0000	------	52.2	0.81	849	111	6.07
.1226	0.0063	51.4	------	------	---	
.2599	.0137	52.7	------	------	---	
.4127	.0216	52.4	------	------	---	
.5605	.0292	52.1	------	------	---	
α-NAPHTHOLBENZEIN IN BENZENE						
0.0000	------	46.1	(1.3)	775	111	5.76
.0751	0.0034	45.3	------	------	---	
.1359	.0064	47.1	------	------	---	
.1840	.0085	46.2	------	------	---	

[a] Figures in parentheses are based upon the estimated partial molar volumes of these compounds and the assumption of ideal mixing.

VI. Discussion

The dipole moments obtained in dioxane are listed in table 2. The conventional formulas for these compounds are also shown. It is evident that the moments of fuchsone and the various hydroxyfuchsones, or benzeins, are unusually large. They range from 5.87 for fuchsone to 7.96 for aurin, and are generally nearly double the values predicted from the component group moments. Resonance involving the normal or conventional structure and highly dipolar structures evidently plays an important part in determining the actual state of these molecules. Of the numerous resonance structures possible, only three representative structures will be illustrated. These are shown for benzaurin in figure 2. Structure I is the normal, or conventional, formula. It should be born in mind that, in addition to structures II and III, a number of other dipolar structures where the positive charge resides on an ortho or para carbon atom of either of the two benzene rings may contribute to the resonance. Important contributions from structures like II might be anticipated because of the gain in Kekulé resonance energy through conversion of a quinoidal ring to a benzene ring.

To determine the effect of resonance on the dipole moments, it is necessary to know approximately the moment of the normal structure alone. Probably the most satisfactory comparison can be made using the moments of the corresponding derivatives of benzophenone. Structurally, the fuchsone differs from the benzophenone having corresponding substituent groups in that the double bond of the keto group is replaced by the

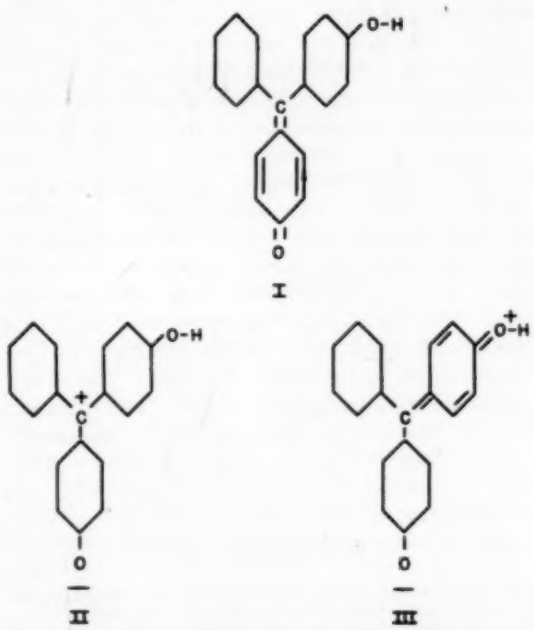
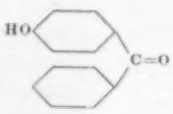
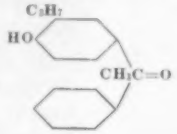
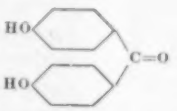
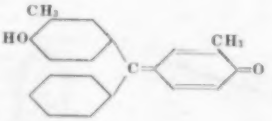
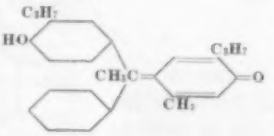


FIGURE 2.—*Most-probable resonant structures for benzaurin, with I, the conventional formula, II and III, the excited dipolar structures.*

quinoidal group. If resonance involving this quinoidal group does not occur, the moments of the corresponding fuchsone and benzophenone derivatives should be about the same. A small difference might be attributed to a change in inductive effects or to a slight shift in valence angles. The relatively large differences actually observed are listed in table 2 under the heading $\Delta\mu$ for the four cases where a direct comparison can be made. Fuchsone was compared with benzo-

TABLE 2.—*Structural formulas, dipole moments in dioxane, μ, and the increments in dipole moments, $\Delta\mu$, attributable to resonance*

Compound	Structural formula	μ	$\Delta\mu$
		esu	*esu*
4-Hydroxybenzophenone		3.96×10^{-18}	
Thymolphenylketone		3.59	
4,4'-Dihydroxybenzophenone		4.49	
Fuchsone		5.83	2.88×10^{-18}
Benzaurin		6.85	2.89
Aurin		7.96	3.47
o-Cresolbenzein		6.70	
Thymolbenzein		6.67	3.08
p-Naphtholbenzein		6.07	

henone, the moment of which was taken as 95 [12].

The dipole moment of fuchsone is 2.9 greater han that of benzophenone. The absence of a ydroxyl group precludes structure III. Because f the many possible dipolar structures that may e involved, a reliable quantitative estimate of he extent of resonance based upon this increment dipole moment cannot be made at present. f the molecule had a fixed dipolar structure as presented by II, the moment estimated from he charge and its distance of separation would be bout 27 as a maximum. Allowance for polariza- on induced in the molecule because of this high paration of charge would lower this estimate. would appear that highly dipolar structures, ch as II, make a contribution of at least 10 rcent, and probably considerably more, to the tual state of fuchsone.

Benzaurin has a moment about 2.9 greater han that for 4-hydroxybenzophenone. This in- ement is practically the same as for fuchsone. he presence of one hydroxyl group does not ppear to enhance the contribution of dipolar ructures to the resonance.

In aurin there is a para hydroxy group in both henyl rings, so that there are possible two quivalent structures corresponding to III. The crease in moment over that for 4,4′-dihydroxy- nzophenone is about 3.5, or 0.6 larger than the crement for fuchsone or benzaurin. A small but gnificant contribution from structures like III indicated.

Thymolphenylketone has a moment 0.37 less han that of 4-hydroxybenzophenone. Only a part f this difference can be attributed to the somewhat wer moment reported for thymol (1.54) [13] than r phenol (1.70) [14]. Steric factors associated ith the two alkyl groups would appear to exert effect. Rotation of the hydroxyl group about he carbon-oxygen bond should be partially re- icted by the adjacent isopropyl group. An effect f this sort has been reported by Smyth [15] from measurement of the moment of 1,4-di-t-butyl-2, -dihydroxybenzene. Completely free rotation of he thymolic ring about the carbonyl carbon-aro- atic carbon bond should also be prevented by teric interaction between its methyl group and the djacent phenyl ring. The net result of these two ctors would be to restrict the relative orientations f the hydroxyl group with respect to the carbonyl group in such a way as to lower the resultant moment of the molecule.[5] This effect can be best illustrated by employing scale models, such as the Fisher-Hirshfelder atomic models.

By comparison with the other hydroxyfuchsones, the moment of 6.07 for α-naphtholbenzein is rather low. Although the moment of the corresponding ketone was not measured, it should not differ greatly from 4-hydroxybenzophenone. The moment of α-naptholbenzein is about 0.8 lower than that of benzaurin, whereas a somewhat larger value might have been predicted for the following reason. Although structure II is less stable than I, this difference is less than it would otherwise be because of the Kekulé resonance energy gained through conversion of the quinoid ring into a benzene ring. Replacing the quinoid by a naphthoquinoid group should give additional stability to structure II by virtue of the increased Kekulé resonance energy of naphthalene over that of benzene. The lower moment might possibly be explained by steric factors that would interfere with the resonance. For convenience only, two of the many possible excited resonance structures were considered in figure 2. A number of additional dipolar structures, not explicitly involving the hydroxyl group, where the resonance extends through more than one ring, are possible. This resonance would tend to bring all rings involved into a coplanar configuration by giving the bond joining each ring to the central carbon atom a partial double-bonded character, and, conversely, this resonance would be inhibited if steric factors interfered with this coplanar alinement. Steric effects apparently prevent three phenyl rings, as in the ion of crystal violet [16], from becoming coplanar, and the effect would be much more pronounced for the larger naphthyl groups.

Thymolbenzein differs structurally from benzaurin only in having a methyl and an isopropyl group in each of the two chromophoric rings. These alkyl groups are para with respect to each other, so that their group moments virtually cancel. The moment is slightly lower than for benzaurin. The difference between the moments of thymolbenzein and thymolphenylketone is, how-

[5] It is immaterial with regard to the resultant dipole moment whether one regards a hydroxyl group attached to an aromatic ring as freely rotating or as existing with equal probability in "*cis*" and "*trans*" positions because of resonance. On the latter basis the lower moment of thymolphenylketone would be interpreted as a steric effect favoring the "*cis*" structure with its lower resultant moment.

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ever, about 3.1, or 0.2 larger than the corresponding increment for benzaurin. Assignment of this increment entirely to resonance is subject to some uncertainty. If steric factors preventing freedom of rotation, as discussed previously, are responsible for the lower moment of thymolphenylketone, the same sort of effect would be operative in thymolbenzein, but its influence on the moment would be different because the presence of the alkylated quinoidal group would limit further the possible relative orientations of the hydroxyl group. Consequently, comparison of the moment of thymolbenzein with that of thymolphenylketone is not quite as direct a measure of the influence of the polar resonance structures as in previous cases. As the increment for thymolbenzein is not very different from that for fuchsone or benzaurin, steric effects of the second type discussed in connection with the lower moment of α-naphtholbenzein and preventing coplanarity of the rings do not appear to be significant in this case. The moment of 6.70 for o-cresolbenzein is influenced to a slight extent by the small group moments associated with the methyl group in each of the chromophoric rings.

The dipole moments of fuchsone, thymolphenylketone, and α-naphtholbenzein in benzene listed in table 1 are 0.03, 0.25, and 0.31 unit lower, respectively, than in dioxane. The appreciable differences for the latter two compounds containing the hydroxyl group can be attributed to the formation of hydrogen bonds with the dioxane.

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Washington, November 27, 1947.

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ational Bureau of Standards

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An Improved Geiger-Counter Arrangement for Determination of Radium Content

By Francis J. Davis

Geiger-counter apparatus in which several counters may be placed in any position relative to each other is described. A circular arrangement of counters to give a counting rate approximately independent of the position of a source near the center of the circle is discussed. The relation of the position of the source to the counting rate of a single Geiger counter is discussed. A method of calculation of the self-absorption of a sample for the Geiger-counter arrangement used is given.

I. Introduction

The usual method of using a Geiger counter for measurement of radium is to use a single unter and to place the sample at some distance m the counter and compare the counting rate th that of a standard in the same position.[1] [2] the measurement of radium samples by this thod, the sample and standard must be ac- rately placed. If the source is at a distance ich is great compared to the dimensions of the unter, the counting rate varies as the inverse uare of the distance. At distances close to the unter, the counting rate varies approximately versely as the distance. For samples of low ntent, which must be placed close to the counter, shape and size of the sample (if different from standard) become important. The different rts of the sample or standard will be at dif- ent distances from the counter, and it becomes ficult to determine the effective distance.

A Geiger-counter arrangement is described in ich the counting rate is independent of the sition of the sample; the only effect of the size d shape of the sample is the change in the rcentage of absorption. A method will be own whereby the absorption can be easily cal- lated for cylindrical samples.

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Method of analysis, AOAC, 6th ed, 663 (1945).

II. Apparatus

The arrangement as originally planned was to use six Geiger counters in a ring. However, four in a square proved adequate. A somewhat similar apparatus was described by H. Neufeldt,[3] who used a counter consisting of two concentric cylinders for the cathodes, with four wires stretched between them as anodes. However, this provides a fixed geometry and sensitivity, limiting the use to samples small enough to be placed in the central cylinder, and also to samples of low radium content that can be counted at a reasonable rate.

The apparatus is shown in figure 1. The counters are in a vertical position and may be placed in any arrangement. They are constructed with outer electrodes of 1-in. copper tubing 10½-in. long and ½₂-in. wall thickness. The center electrode is 1-mil tungsten wire. The filling of the counters is 10 percent of *n*-heptane and 90 percent of argon at a total pressure of 10 cm Hg. A lead shield ½-in. thick surrounds each counter, and the first amplification stage (6C5 tube) is mounted on one end. The high-voltage lead and supply-voltage leads for each counter tube and first amplification stage are in separate shielded cables. The output of the high-voltage supply of approximately −1,000 v is

[3] Hans Neufeldt, Physik. Z. **30**, 494, (1929).

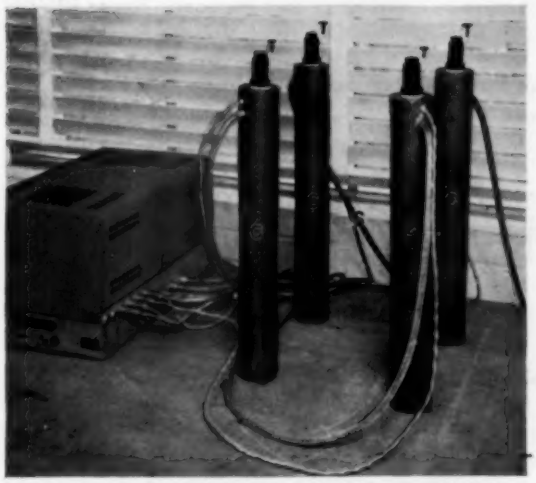


FIGURE 1.—*View of counters and scaler assembled for use.*

P, power supply and scaling circuit; C, Geiger counters encased in ½-in. lead shields; *S*, position of source in the center of the four counters; *T*, first amplification stage (type 6C5 vacuum tube).

regulated by ten $\frac{1}{25}$-watt neon lamps with a 1-megohm resistor in series. The voltage pulses from the 6C5 tubes are fed to a pulse shaper of a biased multivibrator type and thence to a scaler. The scaler is of the hard-vacuum twin-triode type with 6SL7 tubes, giving a scaling ratio of 128. The circuit for the scaler is shown in a previous paper.[4] The mechanical counter used is a telephone message register. The samples are supported either from above by thread or set on a small pedestal. The size of the square arrangement determines the sensitivity. The smallest square, with lead shields touching, is 6.2 cm on a side. This allows a cylindrical sample 2.5 cm in diameter to be placed in the center. For this arrangement the solid angle subtended by the counters from a point source in the center is approximately one-third of the total 4π solid angle. The counters should be tested individually and should have the same sensitivity. In case of slight differences in sensitivity, the two most sensitive should be placed diagonally opposite to give the least variation in counting rate with position of source

III. Effect of Position of Source

A Geiger counter, if uniformly sensitive over the sensitive area independent of the direction of the gamma rays, has a counting rate proportional to the solid angle at the point source subtended by the area. In figure 2 the points *O* and *O'* are the centers of the ends of the cylinder represent the counter cathode, and *XX'* is a line thro the source *S* and parallel to *OO'*. Lines *D* and *CO'B* are arcs of circles generated by rotat *O* and *O'* around the axis *XX'*. Points *A*, *B*, *D* are defined by the intersection of these with the tangent planes *ASB* and *CSD*. solid angle subtended by the cylinder is assum to be bounded by surfaces *ASB*, *BSC*, *CSD*, *DSA*. Conical surfaces *BSC* and *DSA* are g erated by rotating lines *OS* and *O'S* around *XX'*. Throughout the greater portion of solid angle, gamma rays will pass through surfaces of the cylinder. Gamma rays pass through end regions *HADH* and *GBCG* are included in the solid angle, but these gamma r pass through only one surface of the cathode will be approximately compensated by the gam rays passing through the end regions *EADE* *FBCF*, which are within the solid angle and p through only one surface of the cathode. Th end effects become more negligible the longer counter tube compared to its diameter.

The solid angle *W*, which is equal to the included on a unit sphere at *S*, can be shown to

$$W = \frac{4b}{(a^2+b^2)^{\frac{1}{2}}} \sin^{-1} \frac{c}{a},$$

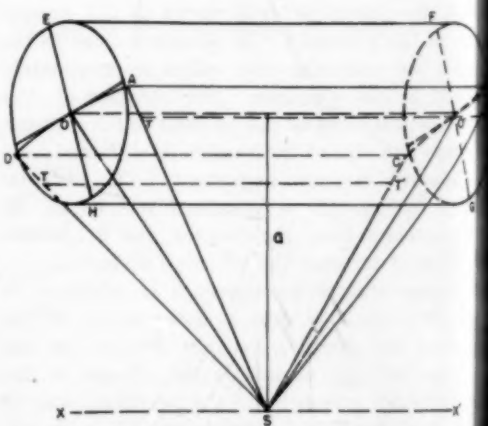


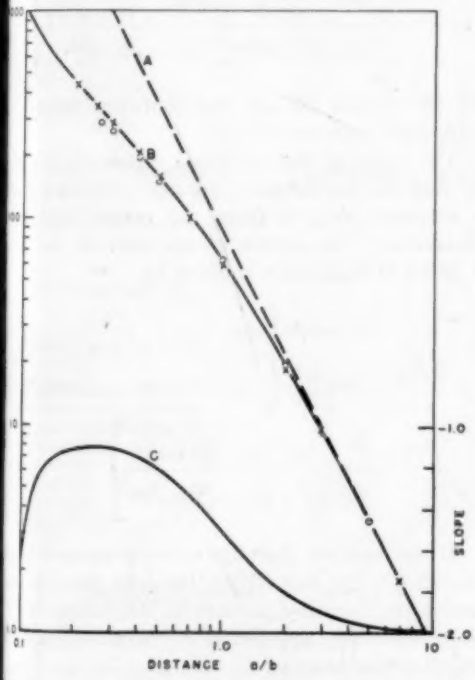
FIGURE 2.—*Diagram of the solid angle at the sour subtended by a counter.*

TT' are the tangent lines of the planes *ASB* and *CSD*; *XX'* is p to *OO'* through source *S*; *DOAS* and *CO'BS* are conical surfaces ge by rotating lines *OS* and *O'S* around axis *XX'*.

[4] L. F. Curtiss and F. J. Davis, J. Research NBS **31** 181, (1943) RP1557.

ere a is the distance from the source to the axis counter, b is one-half the length of the counter, d c is the radius of the counter.

Curve B in figure 3 shows the variation of the oretical relative counting rate with the distance the source from the counter according to eq 1. is curve is for a counter used in the square angement, which has a ratio of half-length to ius (b/c) equal to 11.43. The coordinate scales d are logarithmic. The points shown as sses are the observed counting rates for a source the distances indicated and with the counter hout its lead shield. The observed points, wn as circles, represent counting rates with the e counter in a ½-in. lead shield. Both sets points are fitted to the curve at the point =5. At close distances the observed points ated by circles fall below the theoretical curve. is is probably due to the greater absorption by lead at close distances, where the average h length of the gamma rays in the lead is longer.



URE 3.—*Counting rate versus distance of source from the counter for the counters used.*

ve A represents an inverse square law variation. Curve B, theoretical r counter ratio of half length to radius (b/c)=11.43. The circles and e are observed points for a counter with and without a ½-in. lead shield, tively. Curve C is the slope of curve B (ordinate on the right).

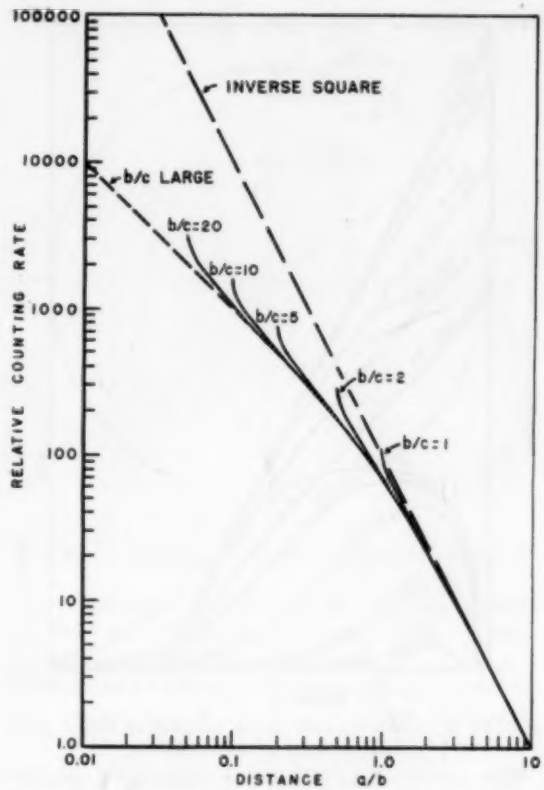


FIGURE 4.—*Counting rate versus distance of source from counter in units of counter half-length.*

a, distance of source from counter; b, half-length of counter, c, radius of counter.

As on log-log coordinates a power function $F=px^q$ has its slope equal to the power q, the slope of the curve B in figure 3 should approach -2 for large values of a/b. A straight line of slope -2 (curve A) is shown for comparison. The calculated slope of the curve according to the function

$$\frac{d \log W}{d \log (a/b)} = \frac{-c}{(a^2-c^2)^{1/2} \sin^{-1} c/a} - \frac{a^2}{a^2+b^2} \qquad (2)$$

is shown by curve C of figure 3. The ordinate of this curve is linear, as shown on the right; the abscissa is the same for the three curves. Any point on the curve then represents the power variation of the counting rate with distance of source. The maximum of the slope curve falls at $a/b=0.24$, with the value -1.10.

In figure 4 are shown several curves for different values of b/c ratio of half-length to radius of

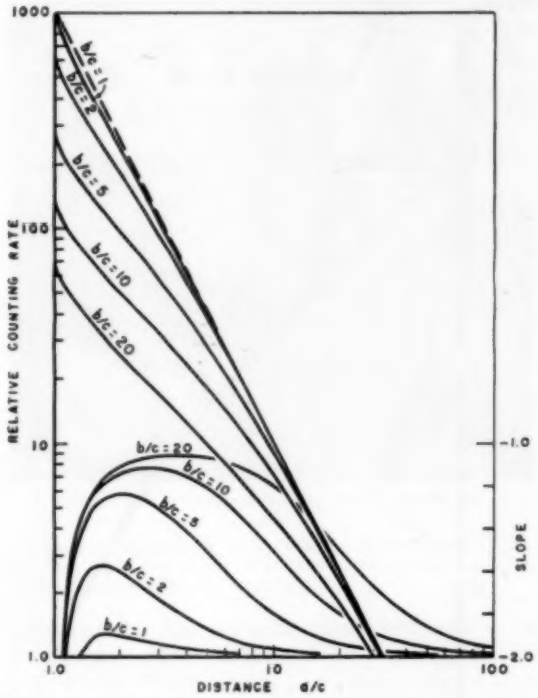


FIGURE 5.—*Counting rate versus distance of source from counter in units of counter radius.*

Upper curves for counters of various ratios of half-length to radius (b/c) Lower curves are the slopes of the upper curves.

the counter. These curves show the theoretical relative counting rate with distance of source in units of the half-length of the counter. It is seen that the smaller the ratio b/c, the more truly the inverse-square law holds. The upper ends of the curves correspond to the position of the source at the electrode. The dotted curved line is the asymptotic line for a counter whose length is very long compared to its diameter. This curve approaches a slope of -1 for small values of a/b.

The curves shown in the upper portion of figure 5 give the theoretical relative counting rate for the source at different distances from the counter in units of the radius (c) of the counter. The curves in the lower portion give the slope of the upper curves, indicating the power relation of the counting rate with distance of source. It is seen that as the source approaches the cathode the slope approaches negative infinity. It would be difficult at very close distances to have an arrangement that would have a counting rate independent of position of the source. For the square arrangement, this region is not accessible because of the ½-in. lead shield, making the closest distance of the source $a/b=0.265$. This is seen to be near the maximum of the slope curve shown in figure

The effect of a vertical displacement of a source within the square arrangement would be the same as for a single counter. Assuming a counting rate N_0 before displacement and a counting rate N_h after a vertical displacement h, the ratio N_h/N_0 derived from eq 1 is

$$\frac{N_h}{N_0}=\frac{(a^2+b^2)^{1/2}}{2b}\left[\frac{b-h}{[a^2+(b-h)^2]^{1/2}}+\frac{b+h}{[a^2+(b+h)^2]^{1/2}}\right]. \quad (3)$$

A horizontal displacement, k, in the direction of a counter of the square arrangement using eq will give a ratio of counting rates

$$\frac{N_k}{N_0}=\frac{(a^2+b^2)^{1/2}}{4\sin^{-1}\frac{c}{a}}\left[\frac{\sin^{-1}\frac{c}{a-k}}{[(a-k)^2+b^2]^{1/2}}+\frac{\sin^{-1}\frac{c}{a+k}}{[(a+k)^2+b^2]^{1/2}}+\frac{2\sin^{-1}\frac{c}{(a^2+k^2)^{1/2}}}{[a^2+k^2+b^2]^{1/2}}\right] \quad (4$$

where N_0 and N_k are the counting rates before and after displacement k.

The ratio of the counting rates N_m/N_0 when N_0 and N_m are the counting rates before and after a displacement, m from the center and in the direction of the center of one side of the square counter arrangement is given by

$$\frac{N_m}{N_0}=\frac{(a^2+b^2)^{1/2}}{2\sin^{-1}\frac{c}{a}}\left[\frac{\sin^{-1}\frac{c}{(a^2+m^2+\sqrt{2}\,am)^{1/2}}}{(a^2+b^2+m^2+\sqrt{2}\,am)^{1/2}}+\frac{\sin^{-1}\frac{c}{(a^2+b^2-\sqrt{2}\,am)^{1/2}}}{(a^2+b^2+m^2-\sqrt{2}\,am)^{1/2}}\right] \quad (5$$

If we assume that the inverse-square law for distance holds (a/b large), the first three terms of series representing horizontal displacements give the following approximate formulas valid for small displacements.

$$\frac{N_k}{N_0}=1+\left(\frac{k}{a}\right)^2+3\left(\frac{k}{a}\right)^4 \quad (6$$

$$\frac{N_m}{N_0}=1+\left(\frac{m}{a}\right)^2-3\left(\frac{m}{a}\right)^4 \quad (7$$

If we assume that the inverse first power law holds, the first three series terms are

$$\frac{N_k}{N_0}=1+\frac{1}{4}\left(\frac{k}{a}\right)^2+\frac{11}{16}\left(\frac{k}{a}\right)^4 \tag{8}$$

$$\frac{N_m}{N_0}=1+\frac{1}{4}\left(\frac{m}{a}\right)^2-\frac{13}{32}\left(\frac{m}{a}\right)^4 \tag{9}$$

A comparison of the results of displacing the source is shown in table 1. The percentage displacement to cause a change of counting rate of 0.1 percent and 1.0 percent is shown in table 2.

TABLE 1.—*Effect of displacement of the source on the counting rate*

Displacement ratio	Ratio of the counting rate after displacement of source over the counting rate before displacement		
	Experimental	Approximate formula	Theoretical
$k/b=0.5$	0.930	.....	0.936
$k/b=1.0$	.763	.....	.770
$k/a=0.2$	1.038	1.045	1.034
$k/a=.5$	1.340	1.438	1.333
$m/a=.2$	1.028	1.035	1.029
$m/a=.5$	1.132	1.062	1.126

TABLE 2.—*Displacement changing the counting rate by 0.1 and 1.0 percent*

Percentage displacement	Percentage displacement required to cause a change of counting rate of 0.1 percent	Percentage displacement required to cause a change of counting rate of 1.0 percent
	Percent	*Percent*
100 k/a, assuming inverse square	3.0	10.0
100 m/a, assuming inverse square	3.0	10.0
100 k/a, assuming inverse first power	6.3	20.0
100 m/a, assuming inverse first power	6.3	20.0
100 h/b at $a/b=0.5$	6.5	20.0
100 h/b at $a/b=1$	5.5	16.5
100 h/b at $a/b=2$	6.0	20.6
100 h/b at $a/b=5$	13.5	42.6

IV. Self-absorption of Sample

To calculate the self-absorption of a cylindrical sample,[6] it is assumed that the gamma rays counted from the element of volume $dxdy$ times the length of sample, shown in figure 6, are parallel to the z-axis, and that the counting rate is independent

[6] C. C. Patterson, J. W. T. Walsh, and W. F. Higgins, Proc. Phys. Soc. 29, 215 (1917).

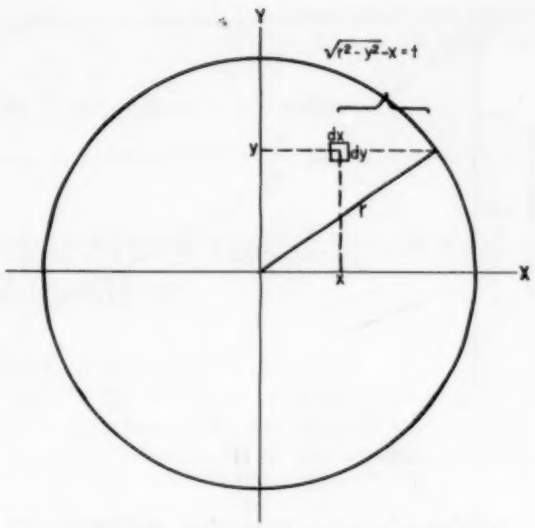


FIGURE 6.—*Diagram for the calculation of self-absorption.*

of the position of the volume element and dependent only on the absorption through the cylinder according to the exponential law $e^{-\mu t}$, where t is the thickness of material through which the gamma ray travels, and μ is the absorption coefficient. If N_0 is the counting rate, assuming no absorption and N_a the counting rate with absorption, then

$$\frac{N_a}{N_0}=\frac{2}{\pi r^2}\int_0^r\int_{-\sqrt{r^2-y^2}}^{\sqrt{r^2-y^2}} e^{-\mu\{(r^2-y^2)^{1/2}-x\}}dxdy$$
$$=\frac{2}{\mu\pi r^2}\int_0^r[1-e^{-2\mu(r^2-y^2)^{1/2}}]dy \tag{10}$$

Expanding the exponential into a series, we have

$$\frac{N_a}{N_0}=\frac{2}{\mu\pi r^2}\left[r-\int_0^r[1-2\mu(r^2-y^2)^{1/2}+\frac{4\mu(r^2-y^2)}{2!}-\frac{8\mu^3(r^2-y^2)^{3/2}}{3!}+\frac{16\mu^4(r^2-y^2)^2}{4!}-\cdots]dy\right]$$

which reduces to

$$\frac{N_a}{N_0}=1-\frac{8}{3}\frac{\mu r}{\pi}+\frac{1}{2}\mu^2r^2-\frac{32}{45}\frac{\mu^3r^3}{\pi}+\cdots$$
$$=1-0.848\mu r+0.5(\mu r)^2-0.2264(\mu r)^3+\cdots.$$

In figure 7 is plotted the theoretical curve N_a/N_0 for various values of μr. Assuming a relation between density and absorption coefficient μ, one can estimate the absorption of an unknown sample by measuring the density to compute μ and obtain the absorption from figure 7.

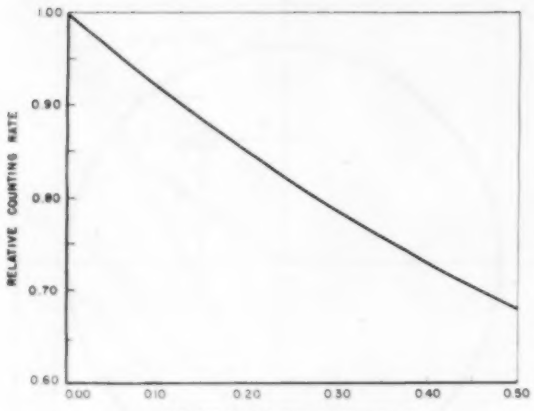


FIGURE 7.—*Relation between self-absorption and radius of ore containers.*

In figure 8 is shown the observed radium content of a sample of high-grade ore concentrate, using different diameters of cylindrical containers and using the method of correction for absorption just given. The points show good agreement with the horizontal line, giving a value of 7.42×10^{-7} gRa/g. Figure 8 also shows a similar curve for a sample of low-grade ore concentrate giving a value of 1.61×10^{-7} g *Ra*/g. This sample was also determined by the radium emanation method giving 1.62×10^{-7} g Ra/g. This method consists of placing the ore in solution and collecting the radium emanation. The amount of radium emanation is then determined by counting the alpha particles emitted by the radium emanation and its short-life decay products and comparing this count with the emanation from a radium standard solution. The apparatus for this method has been described in a previous paper (see footnote 4). The containers used are glass cylinders, and the absorption of the glass is determined by comparing measurements of a source of radium in the glass and without the glass. Estimates of absorption of the standard are made in the same manner as for unknowns.

V. Performance of Apparatus

In the past year the instrument has proved to be useful for rapid analysis. Very few adjustments have been made since its initial construction. The sensitivity of the apparatus when the counters are as close together as possible is such that 0.1 μg of radium will double the background

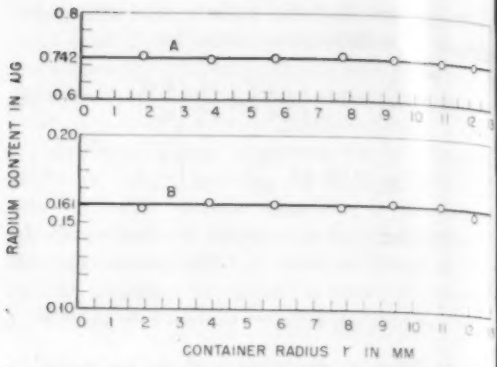


FIGURE 8.—*Observed radium content in containers of various radii.*

A, High-grade ore concentrate; *B*, low-grade ore concentrate.

counting rate. With this value as a minimum and assuming a 100-g sample, the radium content would be 10^{-9} g Ra/g. Estimates can be made of the radium content that gives an increase of the counting rate as low as one-tenth of the background, but no great accuracy of determination can be claimed.

In addition to well-known requirements for statistical accuracy, the following factors limit the accuracy. The ratio of absorption coefficient and density is not a strict constant but may vary as much as 20 percent among light materials. If the absorption of the substance is of the order of 10 percent, the error in the measurement of radium content due to this cause would be of the order of 2 percent. Errors due to assumptions not strictly true in the derivation of the correction for self-absorption would show as a slope or curvature of the horizontal lines in figures 8 and 9. A comparison of determinations made by the method here described with determinations by the radon method showed agreement within 2 percent. Better agreement may be expected if all the materials are of the same nature.

All samples should be sealed for at least 30 days before measuring them unless standard samples of rock or other material are available in a similar condition so that the percentage of radon lost is the same.

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Changes Caused in the Refractivity and Density of Glass by Annealing

By Arthur Q. Tool, Leroy W. Tilton, and James B. Saunders

The changes in the refractivity of several glasses caused by annealing at different temperatures are presented. The results are given in the form of equilibrium temperature coefficients, as the glasses were annealed at each annealing temperature until there was no further change in the refractivity or density. The measurements on refractivity and density were made at standard atmospheric temperatures since the changes in these properties at such temperatures have a greater practical significance than the corresponding changes at temperatures within the annealing range.

I. Introduction

Investigation has shown that the physical properties of a glass depend not only on its actual temperature, but also on the annealing or heat treatment to which it has been subjected [1, 2, 3].[1] It has also been shown that annealing ordinarily causes a glass to approach a condition of equilibrium at the temperature of the annealing treatment. Moreover, the effect of any annealing treatment on the properties of a glass is a function of the change that the treatment has caused in the equilibrium temperature [3, 4, 5].

To determine the change caused in any property by a given change in the equilibrium temperature, it is first necessary to establish equilibrium conditions at a number of annealing temperatures. Also, it is necessary in each case, after equilibrium has been established, to cool the glass to some standard temperature for measurement of the coefficient representing the property under investigation.

Unless the measurements are made at a standard temperature rather than at the temperature of treatment, the results obtained represent effects produced, not only by a change in equilibrium temperature [5], but also by the change in actual temperature. Moreover, the results, even when determined at a standard temperature, will depend on the temperature chosen. This follows because the temperature coefficients of most properties also vary with the equilibrium temperature. For example, it has been shown [6, 7] that both the thermal expansivity and volume of glass increase with the equilibrium temperature. Consequently, the change in volume for a given change in equilibrium temperature is greater when measured at a standard temperature within the annealing range than when measured at atmospheric temperatures.

Refractivity is one of the properties that is changed appreciably, even if the equilibrium temperature is changed by no more than 1 deg C. Any such change in this property of optical glass has considerable practical significance. This is true not only because a difference in the annealing treatments of different portions of glass from the same melt causes the refractivity to vary from portion to portion, but also because unsatisfactory annealing may cause appreciable equilibrium temperature gradients within individual blanks [8, 9]. In other words, these temperature gradients can cause appreciable optical inhomogeneity.

From a practical standpoint, interest centers mainly on the variations that annealing treat-

[1] Figures in brackets indicate the literature references at the end of this paper.

ments cause in the refractivity at atmospheric temperatures, since optical glass is generally used at such temperatures. Lebedeff and Stozarov [10, 11] determined the change in refractivity for several glasses as their equilibrium temperature was changed. However, their measurements of the refractivity were made at the temperatures of treatment. To determine the corresponding indices under atmospheric conditions from such measurements, the average temperature coefficients for the ranges from the treating temperatures to normal atmospheric temperature must be determined for each condition of equilibrium. As these determinations add greatly to the work involved, the measurements at the treating temperatures were not undertaken in procuring the results presented in this or in previous reports [2, 12]. That is, all refractivity and density determinations were made at standard atmospheric temperatures. Recently, MacMaster [13] has reported the results of a similar investigation in which the measurements of the indices were also made only at a standard atmospheric temperature.

To differentiate between the equilibrium and actual temperatures, these temperatures will be designated as τ and T, respectively. Consequently, the coefficients determined in this investigation are designated as $\Delta n_D/\Delta\tau$ and $(\Delta n_F - \Delta n_C)/\Delta\tau$, in which n_F, n_D, and n_C are the indices for the F, D, and C spectral lines respectively. In some cases, the corresponding coefficient, $\Delta D/\Delta\tau$ for the change in density, D, was also determined.

II. Glasses Investigated

Most of the glasses tested in this investigation were from melts of optical glass produced by the Glass Section of the National Bureau of Standards, and they represent practically all the types made in quantity by the Glass Section prior to 1930. The six samples from which prisms were made for measurements on both refractivity and density were mostly from glasses [2] produced after 1920, and the prisms were cut from large selected pieces that, in all cases, were large fragments that resulted when the pots of glass were broken open.

The six selected pieces, before being heat treated, were investigated carefully to determine the magnitude of the refractivity gradients in them. It was found [14] that these gradients ranged from 0.6×10^{-6} to 4.9×10^{-6}/cm, and it is believed that they were chiefly the result of gradients in the equilibrium temperature rather than of variations caused by chemical inhomogeneities or residual elastic strains. Strain was an improbable source of the gradients because the double refraction effects in the large pieces were no greater than they often are in pieces of equal size that have supposedly received adequate annealing, and the effects in the small test samples, that were cut from the large pieces, were presumably negligible. Variations in chemical composition are a possible cause of such gradients as variations of that kind are often the cause of serious optical inhomogeneity; but there is reason to believe that the effect of variations in the chemical composition of the best selected optical glass is very small [15]. Variations in the equilibrium temperature, on the other hand, seem to be a very likely cause of the observed refractivity gradients because τ-gradients, like residual elastic strains, cannot be completely eliminated and also because the refractivity is comparatively very sensitive to differences in τ. In fact, it seems probable that the effects of τ-gradients will usually mask any refractivity gradients arising from variations in the composition of good pieces of optical glass.

Besides the 6 glasses already discussed, 15 additional glasses were subjected to the heat treatments and refractivity measurements required to establish their equilibrium curves. Of these, 14 were also from melts [16] made by the Bureau's Glass Section, and several of them are among those listed in the table of refractive indices that appears in the Smithsonian Tables [17]. One glass, a heavy flint, was of German make and was cut from a Pulfrich refractometer block.

III. Measurement of Refractivity and Density

Of the six glasses on which both refractivity and density were determined, the test prisms were about 40 mm in length, their faces 12 to 16 mm

[2] The composition of melt 494 was determined by analysis. The percentage compositions as given for the other five of these glasses are estimates based on the batch compositions.

Melt 494, SiO_2 50.55, PbO 40.14, Al_2O_3 0.65, K_2O 5.93, Na_2O 2.69, Fe_2O_3 0.02; melt 467, SiO_2 39.0, PbO 54.0, K_2O 6.5, Na_2O 0.5; melt 573, SiO_2 67.5, BaO 2.5, ZnO 1.0, K_2O 10.8, Na_2O 7.2, B_2O_3 11.0; melt 529, SiO_2 74.5, CaO 13.5, Na_2O 12.0; melt 572, SiO_2 48.0, CaO 2.0, BaO 27.0, ZnO 8.0 B_2O_3 5.5, K_2O 7.5, Na_2O 2.0; melt 480, SiO_2 34.5, BaO 40.7, ZnO 7.7, B_2O_3 10.6, Al_2O_3 6.5.

in width, and their refracting angles approximated 60 degrees. Such slender prisms were used to increase the volume for density measurements without making it necessary to reduce the rate of safe cooling after the heat treatments. The average prism of the 14 other Bureau glasses also possessed a refracting angle of about 60 degrees, but its faces were approximately 15 mm square. The prisms of the German glass were much smaller.

A spectrometer was used in measuring the indices of refraction by the minimum deviation method, and the necessary precautions [18] were taken to obtain high precision. Never less than the usual three spectral lines (C, D, and F) were used and, when the dispersion was sufficient, the D_1 line of the sodium doublet was chosen. Repeated measurements on freshly surfaced prisms indicated that variations in the results on any given prism in an unchanged equilibrium condition were small in the sixth decimal place. However, the lack of precision was considerably greater in the intermediate determinations, which were often made without resurfacing the prisms and merely for observing whether equilibrium was almost reached. This lack of precision in the intermediate observations was caused by surface warping and was particularly troublesome after treatments at the higher temperatures, and also after treatments at the lower annealing temperatures if these treatments immediately followed high-temperature treatments.

The density measurements were made by the Bureau's Capacity and Density Section. The usual displacement method of determining volumes was employed, and the submersing liquid was a suitable kerosine held at 20° C. Precautions were taken to minimize the errors caused by the action of surface tension on the suspension wire. Several repetitions of the measurements on the samples after each treatment indicated that the maximum variation in the results on any prism of unchanged equilibrium approximated ± 0.0004 under the worst conditions (comparatively high densities and small volumes).

IV. Heat Treatments

Small tubular electric furnaces (tubes about 50 cm in length and 4 cm in diameter with stoppered ends) were used to treat the glass prisms. To make the temperature distribution within the central third of a furnace more nearly uniform, a heavy-walled metal tube about 15 cm in length was fitted loosely within the refractory tube of the furnace and midway between its ends. The ends of the metal tube were blocked by diaphragms. The junction of a Pt–Pt-Rh thermocouple was placed near the top and midway between the ends of this enclosed space, and the wires of the couple were led through the rear diaphragm and stopper to the cold-junction box. A thin-walled metal capsule containing the glass to be treated was placed just beneath the hot junction. The glass prism within this capsule rested on a thin sheet of burned asbestos to prevent contact with the metal. This arrangement made rapid cooling and heating without breakage possible.

The furnace was brought to a chosen treating temperature before the glass was introduced. Consequently, the glass was heated to this temperature very quickly. After a treatment of the desired duration was completed at any temperature, the glass, still within the capsule, was removed from the furnace and cooled rapidly in air. Except at the highest treating temperatures employed, this procedure allowed very little change in equilibrium temperature during the heating and cooling.

Samples of the same glass were always treated in the same furnace because it was found that the equilibrium temperatures reached in the various furnaces differed by a few degrees, although the treating temperatures as determined by thermocouples were practically identical. This experience indicated errors in the temperature determinations and, presumably, these errors resulted from peculiarities in the furnaces and thermocouples. Generally, the difference between the equilibrium temperatures attained in two furnaces that were supposedly at the same treating temperature did not change materially even when treatments were made at several well-separated temperatures in the annealing range. Thus, it appears that the error in the interval between any two treating temperatures of a glass was always relatively small because the same furnace was used in both cases. It is estimated that the errors in such interval determinations were between ± 2 degrees, whereas the maximum errors in the treating temperatures may have been two or three times as great.

The period of treatment required to establish

equilibrium at low annealing temperatures often exceeded 2 months, while no more than a day was necessary at the highest temperatures used. In many cases, the treatment of a sample at a temperature was repeated one or more times before subjecting the sample to treatment at some other temperature. This repetition of a treatment is one means of determining if an equilibrium condition has been approximated. However, more dependence was placed on the results obtained when it appeared that practically the same equilibrium refractivity or density was reached by increasing it in one case and by decreasing it in another through treatments at the same temperature. The most satisfactory method of accomplishing this opposite approach to an equilibrium condition is the simultaneous treatment of two samples at an intermediate temperature after one has been treated at a higher and the other at a lower temperature.

V. Experimental Results and Discussion

Excepting the highest and lowest treating temperatures employed for any glass, all others were generally within the portions of the annealing ranges that are recorded in tables 1 and 2. Usually, the interval between the chosen treating temperatures was 10 deg C and, as previously indicated, the glasses were made to approach equilibrium at the selected points from both undercooled and superheated conditions. At low-treating temperatures, complete agreement between the results attained by these opposed approaches was difficult to approximate as reducing the interval between the results for the refractivity to 1 in the fourth decimal place usually required treatments of 1 or more months' duration for each direction of approach. At high-treating temperatures, closure of the interval was approximated much more easily because the rates of approaching equilibrium are so much higher than at temperatures in the lower part of the annealing range. In fact, equilibrium is often approached so closely in a comparatively short time that the results show an apparent overlap instead of a gap if the treating temperature is not carefully controlled. In other words, the refractivity measurements after treatments of adequate duration can show an apparent overlapping of 1 in the fourth decimal place if an error of −2 degrees is made in the treating temperature of the undercooled sample, and an equal, but opposite, error is made in the case of the superheated sample. Two samples in different initial conditions were often treated simultaneously in order to prevent such overlapping.

TABLE 1.—*The equilibrium-temperature coefficients of refractivity and density for six glasses*

Glass		Initial condition of glass (glass from pot)			$\frac{\Delta D}{\Delta \tau}$	$\frac{\Delta n_D}{\Delta \tau}$	Temperature range covered by tests
Type	Melt No.	Density [1] 20° C	Refractivity 25° C	Approximate τ-value			
				°C			°C
Medium flint	494	3.3490	1.59000	400	16×10^{-4}	24×10^{-4}	360 to 450
Dense flint	467	3.9320	1.65608	405	27	36	360 to 450
Borosilicate crown	573	2.5305	1.51750	520	29	50	460 to 540
Ordinary crown	529	2.4960	1.52020	525	17	30	500 to 570
Light barium crown	572	3.1587	1.573588	540	33	47	490 to 570
Dense barium crown	480	3.6997	1.62265	605	46	60	560 to 630

[1] The densities, D, were determined by E. L. Peffer and E. E. Hill of the Capacity and Density Section of the National Bureau of Standards.

TABLE 2.—*Equilibrium-temperature coefficients of refractivity for 15 additional glasses*

Glass		Initial condition		$\frac{\Delta n_D}{\Delta \tau}$	$\frac{\Delta(n_F - n_C)}{\Delta \tau}$	Temperature range covered by tests
Type	Melt No.	n_D at 25°C	τ-value			
			°C			°C
Light crown	20	1.51780	464	27×10^{-6}	$+0.6\times10^{-7}$	410 to 510
Do	103	1.51820	448	30	−1.2	410 to 480
Do [a]	123	1.51714	.....	.....	.....	.....
Borosilicate crown	94	1.52002	510	38	−0.7	480 to 540
Do [a]	241	1.52430	519	53	−1.6	480 to 540
Light barium crown	87	1.57340	541	42	−4.6	510 to 560
Do [a]	116	1.57406	539	41	−4.6	510 to 570
Dense barium crown [a]	151	1.61786	579	54	−0.0	540 to 620
Barium flint [a]	135	1.56819	495	36	.0	460 to 530
Do	145	1.55239	493	31	.0	460 to 530
Light flint	33	1.58484	463	23	+2.3	420 to 490
Do [a]	188	1.58038	455	25	+1.4	420 to 480
Medium flint	110	1.62493	426	28	+3.0	380 to 470
Do [a]	163	1.62491	430	27	+3.9	390 to 460
Dense flint [a]	76	1.65548	439	28	+5.3	390 to 460
Very dense flint [b]	.....	1.91794	385	48	+40.0	340 to 400

[a] Glasses listed in Smithsonian Tables, Ed. 7, Rp. 3, p. 277 (1927).
[b] A German product used on Pulfrich refractometers.

Figure 1, which was prepared for a progress report [12],[3] gives a typical representation of preliminary data obtained by these investigations. Figure 2 shows both refractivity and density data obtained on a third glass. The caret-like symbols indicate the indices reached by treating an undercooled glass at various temperatures for periods of treatment that were not always sufficient, and two or more carets at the same temperature indicate that added treatments were given in order to bring about a closer approach to equilibrium. The inverted carets show the indices reached by treating superheated glass at the temperatures indicated until equilibrium was approximated. The trend of the results for different temperatures is indicated by straight lines, as the equilibrium indices are related almost linearly to the treating temperatures as long as these temperatures are confined to that portion of the annealing range covered by the tests. That is, $dn/d\tau$ is approximately constant and can be determined graphically as indicated by the straight lines, A and B, in figure 1. The data on the changes in density indicate that $dD/d\tau$ also is practically constant in most cases (see fig. 2).

These coefficients, so determined both for density and for refraction of the D-line of sodium, are presented in table 1. It is estimated that the maximum error in coefficients is about ± 5 percent. Preliminary data on some of these coefficients have been presented in annual reports of the Director of the National Bureau of Standards [19]. Since then, there has been some revision, and data on the initial condition of the glasses is now included. The usual type-designations that are employed in both tables 1 and 2, are not particularly significant because such designations generally have no unique relation to composition, which is a factor that often varies appreciably even in successive melts of any particular type. Consequently, the coefficients of a number of glasses bearing the same type designation often vary over a considerable range.

Excepting the results for a very dense flint, table 2 presents data obtained on earlier melts made at the National Bureau of Standards. The samples used for five of these melts were those on which the indices appearing in the Smithsonian Physical Tables [17] were obtained. Of the other three Bureau melts for which the indices are given in the Smithsonian tables, the samples used for the earlier index determinations were not available. In one of these cases, melt 123, there was also no duplicate sample, but its composition was about the same as that of melt 103. In the other two cases, melts 151 and 163, duplicate samples were available, but their indices differed

[3] The figure was shown when a preliminary paper concerning this investigation was presented at the Corning meeting of the American Optical Society in 1937, and is similar to an earlier graphical representation shown at the Ithaca meeting of the society in 1925 [2], while demonstrating how the refractivity and density of another glass (NBS melt 494) were changed as the equilibrium condition was changed by annealing at different temperatures.

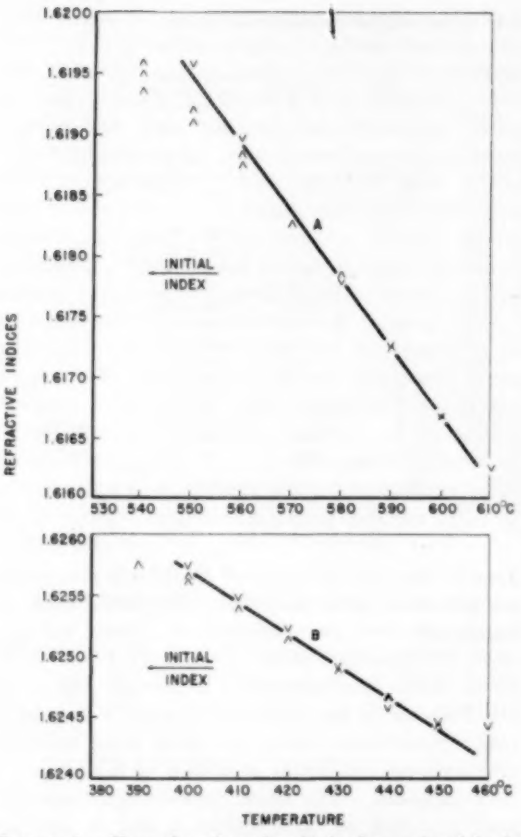

FIGURE 1.—*Examples of results obtained on refractivity by annealing at different temperatures until equilibrium was reached.*

A, results obtained on melt 151. Carets and inverted carets indicate indices reached as the refractivity was being increased and decreased, respectively, by bringing the glass to equilibrium at the temperatures indicated. Two or more carets at the same temperature signify that observations were made before equilibrium was reached. *B*, Similar results on melt 163.

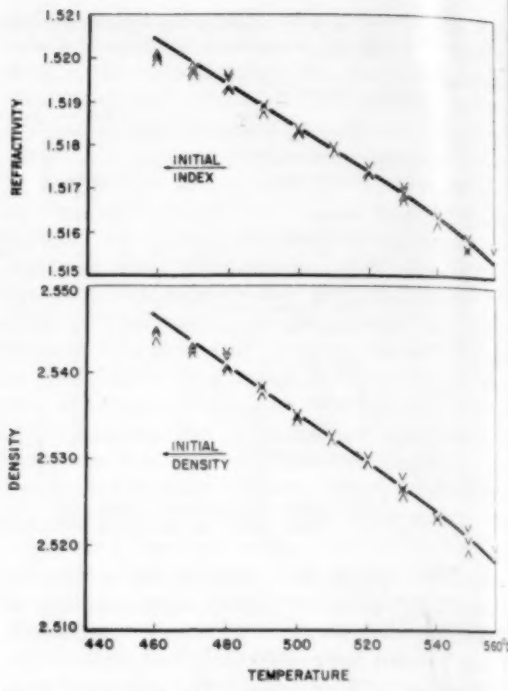

FIGURE 2.—*Results obtained on both density and refractivity of melt 573.*

from those published in the tables. For melt 151, the difference (0.0003) possibly results almost entirely from differences in the annealing. For melt 163, the comparatively large difference (0.00234) suggests a possible error in sample numbers.

The maximum errors in the determinations of the treating temperatures and the coefficients, $\Delta n/\Delta\tau$, are thought to be about the same for table 2 as for table 1. The magnitude of the errors in the determinations of the added dispersion coefficient, $(\Delta n_F - \Delta n_C)/\Delta\tau$, are rather uncertain and, in some cases, are probably large; nevertheless they are apparently insufficient to affect the general trend of the results. As would be expected in view of the relatively large values of $\Delta D/\Delta\tau$ as compared to the ordinary expansivities of the glasses, $\Delta n/\Delta\tau$ is always negative, and the dispersion coefficients are either negative or almost zero whenever, as in crown glasses, the ultraviolet absorption band is so remote from the visible spectrum that a shift of this band plays a secondary role compared to that of the density change in causing changes in refractivity even for blue light. However, in the flints in which there is presumably a comparatively pronounced extension or shift of the absorption band or region toward the visible spectrum as τ increases as well as when T increases, the dispersion coefficients have positive values that are large in dense flints in which the transmission for blue light is reduced appreciably because of the proximity of the absorption region.

The relations of the equilibrium temperature coefficients of refractivity and dispersion to the coefficient $\Delta D/\Delta\tau$ and to the shift of the ultraviolet absorption band as τ changes are clarified greatly

by a consideration of Pulfrich's results on the ordinary temperature coefficients of refractivity and dispersion for glasses in the range from 0° to 100° C. Pulfrich's results [20] suggest that dispersion coefficients, such as $\Delta(n_F - n_C)/\Delta T$, are always positive, although the coefficients $\Delta n/\Delta T$ may be either positive or negative, depending on the kind of glass and the temperature range. Obviously, the decreasing density of a glass as it heats would result in negative temperature coefficients for both refractivity and dispersion if there was no absorption band effect. Moreover, it is well known that the proximity of the ultraviolet absorption region to the visible spectrum considerably increases the refractivity, especially for light near the short wavelength end of the spectrum, and also that the relative increase in refractivity for shorter wavelengths becomes greater as the absorption region moves toward the visible spectrum because of an increasing temperature. Thus, Pulfrich explained his results on the assumption that, as T increases, the negative effects of decreasing density are opposed by the positive effects caused by the proximity of the ultraviolet absorption region to the visible spectrum and by the shift of this region toward longer wavelengths as T increases.

According to this explanation, the effects attributed to the absorption region and its shift with temperature generally overshadow those caused by the change in density. Ordinarily, the ultraviolet region is nearer the visible spectrum in flints than in crowns, and it actually encroaches upon it in some cases. As a result, the temperature coefficients of dispersion and refractivity are positive in flints and generally larger than in crowns. Although smaller, those of the latter glasses are, with some exceptions, such as the negative coefficients of refractivity found by Pulfrich, also positive. That all of the glasses tested in the present investigation have negative equilibrum temperature coefficients, such as $\Delta n_D/\Delta\tau$, and that many of the crowns also have negative dispersion coefficients, such as $\Delta(n_F - n_C)/\Delta\tau$, must be ascribed to the fact that $\Delta D/\Delta\tau$ is usually much larger than $\Delta D/\Delta T$, and also to the probability that changes in τ cause smaller shifts in the ultraviolet absorption region than are caused by equal changes in T, even if the latter changes are confined to the range between 0° and 100° C.

VI. Summary and Conclusions

Results for the equilibrium temperature coefficients of refractive index, dispersion, and density were determined for several different optical glasses.

The range of equilibrium temperatures covered was, on the average, about 70° C for each glass, and this range comprised most of the annealing range that is usable for optical glasses.

Excepting at the end temperatures of this range, the equilibrium temperature was approached both from above and below and, within the errors of measurement, the same results were obtained in both cases.

The time required to establish equilibrium ranged from several months at low annealing temperatures to only a few hours at the highest employed.

To have employed higher temperatures would have required much smaller samples because the cooling from such temperatures must be very rapid if a downward drift of the equilibrium temperature is to be prevented. Such very small samples necessitate the use of less accurate methods for refractivity and density measurements.

By cooling to normal (atmospheric) standard temperatures, the results obtained have a more practical significance than those made at higher temperatures, because it is in the range of atmospheric temperatures that optical glass is ordinarily used.

From the results obtained, it was concluded that the density and the refractivity for any wavelength of light increase almost linearly as the equilibrium temperature decreases; therefore, the equilibrium temperature coefficients of both density and refractivity are negative and practically constant.

The average magnitudes of the equilibrium temperature coefficients of density, and of refractivity for the D-line, are about 28×10^{-6} and 37×10^{-6}/deg C, respectively, and both are large enough to cause undesirable inhomogeneity even if the gradients in this temperature exceed no more than a tenth of a degree per centimeter in any glass of which exceptional homogeneity is required.

From the results obtained, it appears that the equilibrium temperature coefficients of dispersion

are usually negative in crown glasses and positive in flint glasses. This difference in the dispersion coefficients doubtless is related to the location of the ultraviolet absorption band which, in heavy flints, often encroaches on the visible spectrum.

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Conductimetric Titrations of Acids and Bases in Benzene and Dioxane

By Arthur A. Maryott

Acid-base titrations were made conductimetrically in pure benzene and dioxane with picric, trichloroacetic, and camphorsulfonic acids, together with primary, secondary, and tertiary amines. Although the conductances of the solutions were extremely low, lower by a factor of 10^{-6} or more than in water, the titrations gave sharp end points which generally were accurate to 1 percent or better. The unusual, though similar behavior of all titrations involving trichloroacetic or camphorsulfonic acid, where the conductance of the salt was enhanced greatly by the presence of free acid, was interpreted in terms of a reaction between salt and acid leading to the formation of a complex anion. The occasional variations in conductance with time, in one instance suggesting slow attainment of some secondary ionic equilibrium, and the effect upon the titration curves of the addition of a small amount of methyl alcohol to the solvent are discussed.

I. Introduction

While the conductimetric method has been employed as a general procedure for acid-base titrations in water and has been extended to certain nonaqueous and mixed solvents, its application to purely nonpolar solvents such as benzene and dioxane which have very low dielectric constants remains practically an unexplored field. One case has been reported by La Mer and Downes [1] [1] in which trichloroacetic acid was titrated with diethylamine in benzene. The titration curve shown by these workers exhibited an interesting and rather unexpected behavior. On titration of the acid with the base, the conductance first rose to a maximum well before the equivalence point was reached and then decreased to a minimum somewhere in the vicinity of the equivalence point. It was not apparent from their data, however, whether there was any definite break in the titration curve at the equivalence point which would be suitable for analytical purposes. The present work was undertaken not only to explore the possibility of extending an analytical method, but also in the hope that additional information concerning the behavior of electrolytes in these media might be obtained.

In solvents like benzene which serve primarily as inert diluents, dilute solutions of acids or bases have almost negligibly low conductances. There is practically no tendency for the solvent to react with the acid or base to form ions as would be the case in an amphoteric solvent like water. When the solution contains both acid and base, however, they combine with the transfer of a proton from the acid to the base [2] to form a true salt. Since the solvent has a low dielectric constant and has little tendency to stabilize individual ions through solvation, the extent of dissociation of the salt into free, or conducting, ions is quite small. The behavior of certain types of organic salts, particularly the tertiary and quarternary ammonium halides and picrates, have been extensively investigated by Walden [2] and by Kraus [3] and coworkers. The very low conductances of these solutions indicate that only a minute fraction of the salt, something of the order of a millionth of 1 percent, is dissociated into free ions. The remainder exists as nonconducting ion pairs, or aggregates of ion pairs, held together largely by coulomb forces. Although the equivalent con-

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] The definition of acid employed here is that of Brönsted rather than the more generalized electronic concept of Lewis. Although compounds owing their acidity to an electron deficiency can be titrated with the aid of colored indicators, these acids are not suitable for the present purpose since an ionic product having a measurable conductance is required.

ductance varies in a rather complex manner with concentration, and suggests a multiple series of equilibria involving the formation of triple ions and more highly associated ionic products, the specific conductance increases continually with concentration. Conductimetric titrations in these solvents might be expected to follow a simple pattern. The extent of ionization of the salt, though small, should be considerably greater than that of either the acid or the base, so that the conductance would be determined almost entirely by the concentration of salt formed. Then the conductance would be expected to increase more or less uniformly until the equivalence point is reached, and remain substantially constant upon the addition of excess titrating solution. It is evident from the experimental results that only a part of the titrations conform to this simple pattern.

The choice of acids and bases is limited by the solubility, particularly of the salt formed, and by the requirement that they be sufficiently strong to insure complete neutralization. In these respects picric and trichloroacetic acids together with various aliphatic primary, secondary, and tertiary amines were for the most part suitable. Titrations were generally made in both dioxane and benzene. To determine the effect of a small amount of polar impurity, in some cases approximately 1 percent of methyl alcohol was also added to the solvent before titrating. Camphorsulfonic acid was used in several titrations in dioxane. Good breaks in the titration curves, corresponding to the equivalence points calculated from aqueous standardizations of the various solutions, were observed in practically all cases.

II. Materials

Reagent-grade trichloroacetic acid was stored in a vacuum desiccator until used. Picric acid and *dl*-camphor-sulfonic acid were recrystallized, respectively, from benzene and dioxane, and dried in a vacuum oven. The various amines, obtained from Eastman Kodak Co., and Sharples Chemicals, Inc., were used without additional treatment. To remove moisture the solvents, benzene and dioxane, were refluxed and distilled over sodium.

III. Apparatus and Procedure

A direct-current, high-resistance bridge, General Radio Co. type 544-B, was used to measure the resistances of the cell during the titrations. These resistances were of the order of 10^7 to 10^{10} ohms. Sensitivity as well as convenience and rapidity of measuring these high resistances, rather than accuracy, were determining factors in selecting the method. Throughout the required range, the resistances could be determined to 1 percent which is as precisely as the logarithmic dial could be read. The use of direct current introduces the possibility that the measured resistances may be influenced by the effects of electrode polarization. Should these effects cause the resistance of the cell to vary appreciably with time, they might interfere with the titrations. In a majority of cases, either no such drifts were observed or else they were sufficiently small so as not to interfere with detection of the equivalence points.

A photograph of the cell and titrating assembly is shown in figure 1. The cell consists of an inner

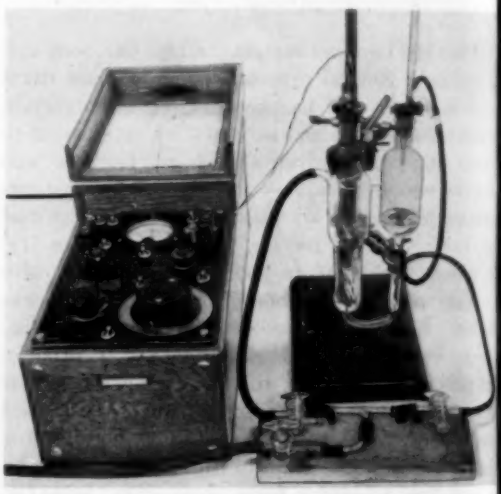


FIGURE 1.—*Assembly used in conductimetric titrations in benzene and dioxane.*

section of soft glass, on which are mounted two concentric platinum electrodes and their leads, and an outer U-shaped container of Pyrex glass.

the cell was also used in measurements of dielectric constants, the lead from the outer electrode is tubular and serves as a shield for the lead from the inner electrode. In addition to the electrode compartment, the outer section contains two enlarged bulbs to accommodate excess liquid and to facilitate mixing the solutions in a manner to be described. The electrodes are 4 cm high, with the outer one having a diameter of 2.4 cm. The spacing between electrodes is approximately 0.2 cm. A sufficiently good estimate of the cell constant, k, is obtained from the parallel-electrode capacitance, C, by the formula, $d/A=1/(4\pi C)$. This capacitance in air, determined by calibration with pure benzene, is 27.4 cm, so that $k=0.00291$ cm^{-1}.

Stock solutions were made up in volumetric flasks from weighed quantities of acid or base so that the concentrations were approximately 0.2 molar. To the cell containing 100 ml of solvent was added 5 ml of stock solution of acid (or base) from a pipette. This solution was then titrated with a stock solution of base (or acid) from a 10-ml burette. The concentration of salt at the equivalence point was thus around 0.009 molar in all cases. As the titrating solution was roughly twenty times as concentrated as the solution to be titrated, the effect of dilution was minimized. Compressed air, dried by passage through a tube containing calcium chloride, was used to achieve mixing upon each addition of the titrating solution by first forcing the solution into one of the enlarged bulbs and then into the other. The burette was attached to the cell opening through a cork stopper, which also contained a tube passing to the compressed air line. With the cell virtually airtight, any danger of contaminating the solution with atmospheric moisture, which might affect the conductance during the titration, was eliminated. Very small additions of stock solution, not over three or four drops, were made near the equivalence point. Whether such small additions were necessary depended upon the shape of the titration curve. In some cases the curves were substantially linear over an appreciable region on either side of the equivalence point, while in others the marked curvature of the plots required that evaluation of the end point be based upon points within a rather limited region.

All titrations were made at 25°±0.01° C in an oil bath. This close control of temperature maintained constant conditions for comparative purposes, and the titrations could be made satisfactorily at ordinary room temperature. The time required to obtain a complete titration curve was about 20 minutes. Because of uncertain purity, particularly of the bases, and in order to have a check upon the reliability of the conductimetric end points, all stock solutions were standardized with aqueous solutions of sodium hydroxide and hydrochloric acid, using phenolphthalein and methyl red as indicators. Solutions of amine in benzene were added to excess acid and back titrated with alkali to eliminate loss of amine through volatilization from the benzene layer.

IV. Experimental Results

A number of preliminary titrations were made using a variety of amines with picric acid or trichloroacetic acid in benzene. While the general shapes of the titration curves were found to be dependent upon the acid, and in some cases, upon the class of amine, no essential qualitative difference was noted within a particular class of amine. Consequently, in the titrations reported, only triethylamine, di-*n*-butylamine, and *n*-heptylamine representing, respectively, the tertiary, secondary, and primary classes of amines were used. Frequently, both forward and reverse titrations were made. The forward titrations are defined as those in which the base is added to the acid, and the reverse titrations as those in which the acid is added to the base.

While representative data for several of the titrations are given in table 1, it seemed generally preferable to present the results in graphical form.

The various titration curves plotted on semi-logarithmic paper are shown in figures 2 to 6. Figures 2 to 5 show forward titrations on the left side and reverse titrations on the right. The specific conductance is plotted on the logarithmic scale. Plotted as abscissa is the function X, defined by $X=(B-A)/D$. A, represents the equivalents of acid, and B, the equivalents of base in the solution at that particular point in the titration. D, is the equivalents of acid or base initially to be titrated and is thus identical with A for the forward and with B for

the reverse titration. The values of A, B, and D are based upon the concentrations of the stock solutions determined by the aqueous standardizations. Up to the equivalence point, X measures the fraction of acid or base not yet neutralized, and beyond this point the fractional degree of overtitration. The forward titrations start with negative values of X, and the reverse titrations with positive values. The equivalence point corresponds to $X=0$.

TABLE 1.—*Representative data on conductimetric titrations*

Forward titration			Reverse titration		
Base added	X	Specific conductance	Acid added	X	Specific conductance
ml			ml		
1.50	−0.698	0.39×10^{11}	1.50	0.702	0.59×10^{11}
3.00	−.396	1.16	3.00	.403	1.40
3.50	−.296	1.53	4.00	.205	2.06
4.00	−.195	1.91	4.25	.155	2.26
4.25	−.145	2.12	4.50	.105	2.46
4.50	−.094	2.36	4.75	.056	2.64
4.60	−.074	2.45	4.90	.026	2.74
4.70	−.054	2.53	4.98	.010	2.85
4.80	−.034	2.63	5.09	−.011	2.91
4.90	−.014	2.72	5.17	−.028	2.91
5.00	.006	2.78	5.26	−.045	2.91
5.10	.025	2.78	5.50	−.092	2.91
5.20	.045	2.80	6.00	−.193	2.88
5.30	.066	2.81			
5.50	.106	2.85			
6.00	.207	2.97			
II. Titrations with trichloroacetic acid (0.1904 molar) and triethylamine (0.1939 molar) in dioxane.					
1.00	−0.806	0.044	1.00	0.794	0.033
2.00	−.611	.092	2.00	.588	.036
3.00	−.416	.114	3.00	.383	.049
4.00	−.222	.180	4.00	.177	.074
4.25	−.172	.180	4.25	.126	.081
4.50	−.124	.174	4.50	.074	.090
4.75	−.076	.159	4.75	.023	.101
4.83	−.060	.150	4.81	.010	.104
4.90	−.047	.142	4.87	−.002	.110
4.98	−.031	.130	4.93	−.015	.123
5.07	−.014	.116	5.00	−.029	.139
5.15	.002	.109	5.06	−.040	.161
5.23	.017	.108	5.12	−.054	.178
5.50	.070	.107	5.25	−.080	.197
6.00	.167	.107	5.50	−.131	.285
			6.50	−.337	.415

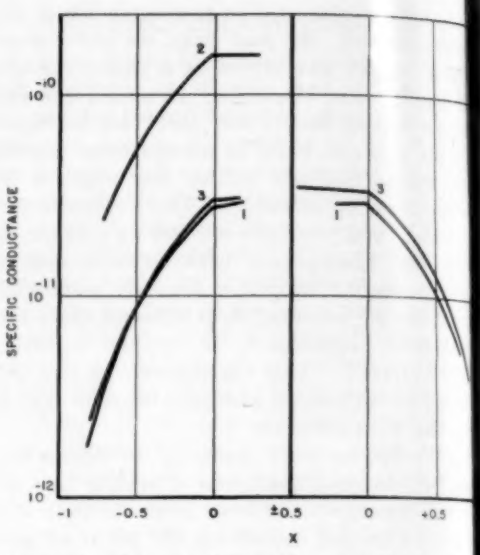


FIGURE 2.—*Forward (left) and reverse (right) titration curves with picric acid and di-n-butylamine.*

Curves: 1, in benzene; 2, in benzene containing 1 percent of methyl alcohol; 3, in dioxane.

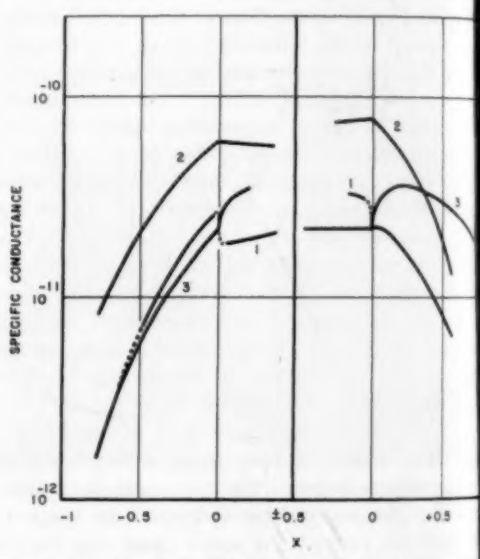
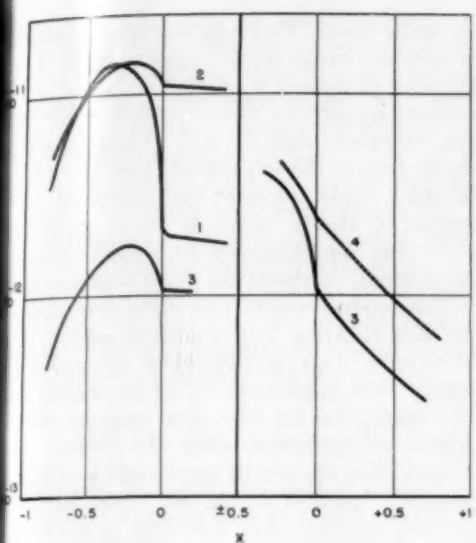


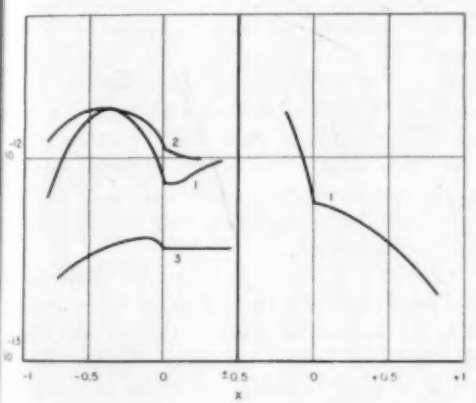
FIGURE 3.—*Forward (left) and reverse (right) titration curves with picric acid and triethylamine.*

Curves: 1, in benzene; 2, in benzene containing 1 percent of methyl alcohol; 3, in dioxane.



URE 4.—*Forward (left) and reverse (right) titration curves with trichloroacetic acid and triethylamine.*

rves: 1, in benzene; 2, in benzene containing 1 percent of methyl alcohol; dioxane; 4, in dioxane containing 1 percent of methyl alcohol.



URE 5.—*Forward (left) and reverse (right) titration curves with trichloroacetic acid and di-n-butylamine.*

rves: 1, in benzene; 2, in benzene containing 1 percent of methyl alcohol; dioxane.

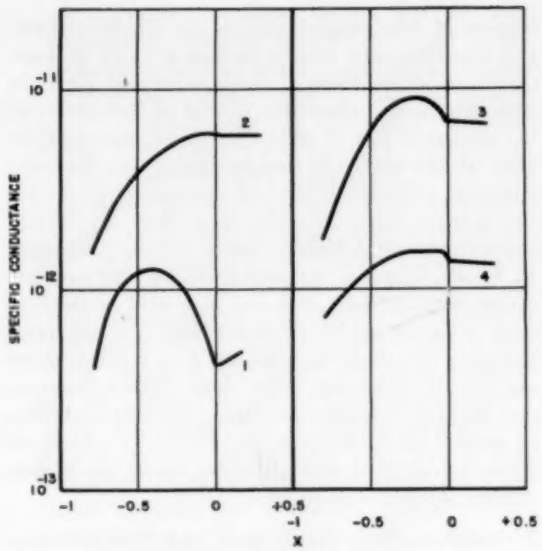


FIGURE 6.—*Forward titration curves using trichloroacetic acid (left) and camphorsulfonic acid (right).*

Curves with trichloroacetic acid and n-heptylamine: 1, in benzene; 2, in benzene containing 1 percent methyl alcohol. Curves using camphorsulfonic acid in dioxane: 3, with triethylamine; 4, with di-n-butylamine.

1. Titrations With Picric Acid and Di-*n*-butylamine

Curves representing the titrations with picric acid and di-*n*-butylamine are shown in figure 2. Those numbered 1, 2, and 3 are the titrations in benzene, in benzene containing 1 percent by volume of methyl alcohol, and in dioxane, respectively. Conductances of the initial solutions containing only free acid or base are not shown on the plots. These conductances were less than one-hundredth the conducance of the salt at the equivalence point. All curves, both for the forward and reverse titrations, have the same general shape and show a pronounced break at the equivalence point. The conductance increases continually until the equivalence point is reached and remains substantially constant thereafter. This is the typical behavior in cases where the conductance is largely determined by the concen-

tration of salt formed during the neutralization, and the titrations bear a formal analogy to conductimetric titrations of weak acids and bases in aqueous media, where the extent of ionization of the acid and base is relatively small compared to that of the salt. A comparison of the forward titration curve with the corresponding curve for the reverse titration shows that they are nearly superimposable. Unlike many of the titrations to follow, there is no indication of any specific interaction between salt and free acid or base of such a nature as to influence markedly the conductance of these solutions. The conductances are not very different in the two solvents, benzene and dioxane, and the addition of the small amount of alcohol to the benzene has merely the expected effect of shifting the titration curve to higher values of conductance.

2. Titrations With Picric Acid and Triethylamine

When similar titrations, shown in figure 3, are made with picric acid and triethylamine rather than di-*n*-butylamine, the results are quite different and dependent upon the solvent. Curves 1, 2, and 3 are again the titrations in benzene, in benzene containing 1 percent of methyl alcohol, and in dioxane, respectively. With the first additions of base during the forward titration in benzene, the conductance is unstable and tends to drift rapidly with time toward higher values. As the titration proceeds, these drifts become less pronounced and practically vanish after somewhat more than half of the acid is neutralized. The conductance then steadily increases in the expected manner until a second drift, this time toward decreasing conductance, occurs at or very close to the equivalence point. The reverse titration shows a corresponding drift toward increasing conductance in the immediate vicinity of the equivalence point, but none during the initial part of the titration. The regions of marked instability are indicated by the dotted portions of the curves.

From a comparison of the forward and reverse titrations it would appear that there are two quite different values representing the conductance of triethylammonium picrate. The conductance near the equivalence point when approached from the forward titration is about 20 percent greater than for the reverse titration, although the concentration of salt is about 10 percent greater in the latter case. To study this effect further a to ascertain which is the proper valu for the c ductance of the salt, a solution of purified trieth ammonium picrate, approximately 0.009 mol was introduced into the cell. Upon the addit of one drop of the solution of picric acid, the c ductance began to drift and continued until reached a steady value in about 10 minut which was approximately 30 percent higher th the original. Subsequent small additions of a did not produce any further drifts in conductan On back titrating with the stock solution of t ethylamine to give a drop excess, the conductan drifted back approximately to its original val This change was not dependent upon the contin passage of current through the solution. It evident from the above experiment and from t instability noticed during the initial part of t forward titration that this drift in conductan toward abnormally high values is associated w solutions containing both salt and free picric ac The process is reversible and possibly suggest slow attainment of some ionic equilibrium inve ing a reaction between the acid and the salt. T possibility that relatively slow reactions may oc in such solvents has been suggested by Dietz a Fuoss [4], who found that the conductances mixtures of tributylammonium chloride and l abietate in toluene drifted with time in a man which indicated a slow ionic reaction betwe these two salts. The failure of larger excesses picric acid to produce additional drifts indicate saturation effect requiring only a very small c centration of acid.

Curves 2 in figure 3 represent titrations w the same solutions, the difference being that 1 p cent by volume of methyl alcohol was added the benzene before titrating. Unlike the tit tions in pure benzene, no drifts in conductan were noted during any part of either the forw or reverse titrations. The shapes of both curv are similar and now resemble those obtained w picric acid and di-*n*-butylamine.

Still different behavior is shown by the tit tions in dioxane. The conductance during t forward titration, instead of leveling off beyo the equivalence point, increases at a faster r than before. In the reverse titration the condu tance reaches a maximum value when only abo 80 percent of the base has been neutralized a then decreases rather rapidly up to the equi

lence point. Beyond this point the conductance remains practically constant. Conductances were stable throughout the titrations. In view of the relatively low conductance of the base, the conductance of solutions containing both salt and free base are unexpectedly high. The conductance at the maximum of the reverse titration is 3.7×10^{-11} compared to a value of 1.4×10^{-11} at the corresponding point in the forward titration where the concentration of salt is the same. There is evidently some rather strong interaction between the salt and base in dioxane of such a nature as to increase markedly the extent of ionization over that produced by the salt alone.

3. Titrations With Trichloroacetic Acid

Figures 4, 5, and the left side of figure 6, show the curves for titrations with trichloroacetic acid. All curves for the forward titrations are qualitatively similar. They rise to a maximum between half neutralization and the equivalence point. Immediately beyond the equivalence point, the conductance tends to level off so that breaks in the curves at the equivalence points are very pronounced. Curves for the forward and reverse titrations have entirely different shapes. The conductance increases throughout the reverse titration but at a faster rate beyond the equivalence point than before. The breaks, though not so striking as in the case of the forward titrations, are still quite definite.

It is apparent from these curves that solutions containing free acid as well as salt have abnormally high conductances. The outstanding illustration is the titration of trichloroacetic acid with triethylamine, curve 1 of figure 4. The maximum occurs at $X=0.3$, which corresponds to a solution containing 0.0065-molar salt and 0.0027-molar acid. The specific conductance of this solution is about 1.5×10^{-11}, whereas that at the equivalence point corresponding to a substanially higher salt concentration of 0.0090 molar is only 2.0×10^{-12}. The drop in conductance just before the equivalence point is extremely sharp. On titrating the last 5 percent of acid there is a threefold drop in conductance. This behavior suggests a specific reaction between acid and salt leading to much greater ionic dissociation than can be attributed to the ordinary dissociation of the salt itself.

In several instances, excess base causes an appreciable increase in conductance. For example, the forward titration curves for trichloroacetic acid with di-*n*-butylamine and *n*-heptylamine in benzene, curve 1 in figure 5, and curve 1 in figure 6, respectively, show a gradual rise in conductance beyond the equivalence point. Some interaction between salt and base is indicated, but the effect is relatively less important than in the case of acid and salt, and is insufficient to cause a maximum in the curve for the reverse titration.

The maxima in the forward titrations are more pronounced in benzene than they are in dioxane or in benzene containing the small amount of alcohol. A comparison of the titrations of trichloroacetic acid with *n*-heptylamine in benzene and in benzene containing 1 percent of methyl alcohol, curves 1 and 2, respectively, in figure 6, shows that addition of alcohol has nearly eliminated the maximum and all but obsecured the end point. The effect of adding alcohol to dioxane is shown for the reverse titrations with trichloroacetic acid and triethylamine. The titration in pure dioxane is represented by right-hand curve 3 in figure 4, and that after the alcohol had been added by curve 4. In the latter case, the end point is much less pronounced, and it would probably not be evident at all upon the addition of somewhat larger amounts of alcohol.

4. Titrations With Camphorsulfonic Acid

The very limited solubility of camphorsulfonic acid precluded its use in titrations in benzene at the desired concentration. Two titrations were made in dioxane, using triethylamine and di-*n*-butylamine, curves 3 and 4 in figure 6, respectively. The appearance of maxima in these curves, just as in the titrations with trichloroacetic acid, shows a similarity in behavior of the two acids.

5. Accuracy of End Points

Except for the titrations with picric acid and triethylamine in pure benzene, the end points were determined by the intersection of smooth curves, usually linear, drawn through points immediately on each side of the break in the titration curve. Agreement with the equivalence points calculated from the independently determined concentrations of the stock solutions was within 3 percent in every case. The average deviation was somewhat

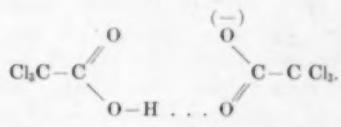
less than 1 percent and within the experimental uncertainties. In the special case of titrations with picric acid and triethylamine in benzene, the end point was indicated by the previously described drift in conductance which was evidently confined to a region within 1 percent of the true equivalence point. Because of the nature of the end point, however, this particular titration is less suitable than the others; and it is apparently not applicable to certain other tertiary amines. Preliminary titrations with tributylamine or triamylamine, although qualitatively similar to those with triethylamine, gave a slower and less pronounced drift in conductance, which did not give a satisfactory indication of the end point. Although the effect of alcohol was not studied in these preliminary titrations, its addition would, in all probability, improve the titrations in the manner observed with triethylamine.

V. Discussion

It is apparent from the various graphs that the titrations, with the exception of those with picric acid and triethylamine in pure benzene, follow one of two general patterns. The simplest type includes all the titrations involving picric acid and di-*n*-butylamine, and those with picric acid and triethylamine in benzene containing the small amount of alcohol. Corresponding curves for the forward and reverse titrations have the same general shape, and the conductance is controlled almost entirely by the concentration of salt formed during the neutralization. For the second type, curves for the forward and reverse titrations have entirely different, though complementary, shapes. In all forward titrations employing trichloroacetic acid or camphorsulfonic acid, the conductance passes through a maximum well before the equivalence point is reached. This maximum occurs in the reverse titration in the particular case involving picric acid and triethylamine in dioxane. Except in the titrations with picric acid and triethylamine, the character of the curves did not depend upon the solvent used.

In order to account for the behavior of titrations of this second type, some specific reaction between salt and acid, or between salt and base in one instance, would seem to be required.[3] Although independent data in dilute solutions are lacking, amine salts of carboxylic acids do form complexes with excess acid under certain conditions. Ralston [5] has obtained evidence from the freezing point diagram of the system, octadecylamine-acetic acid, of the presence not only of the 1:1 compound representing the simple salt but also of a compound containing two molecules of acid to one of base. Prideaux [6] found that the conductance of the two component system, diethylamine-propionic acid, when corrected for changes in viscosity had a maximum value in the neighborhood of 70 mole percent of acid, and concluded that a complex salt having a higher conductance than the simple salt was formed.

That carboxylic acids associate into dimers through the formation of hydrogen bonds in the vapor phase and in solvents like benzene is well established [7]. The reaction between simple salt and acid, formulated by $HB^+ \ldots A^- + HA = HB^+ \ldots HA_2^-$, might be attributed to the formation of a complex anion having a similar structure except that only one hydrogen bond could be formed. For the case of trichloroacetic acid, this structure would be represented by

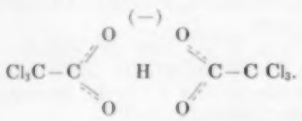


Formation of such a complex salt would be expected to enhance the conductance of the solution. The larger size of the complex anion and the better shielding of its charge should lead to a higher degree of dissociation of ion pairs into free ions, than for the simple salt, by diminishing the attractive forces between the oppositely charged ions.

It is interesting to note that the reaction between acid and salt still takes place when dioxane rather than benzene is the solvent. Dioxane, like other solvents the molecules of which contain acceptor atoms, tends to destroy hydrogen bonds

[3] The high conductances of solutions containing salt and acid together were noted by La Mer and Downes in the titration of trichloroacetic acid with diethylamine in benzene, previously mentioned [1]. These authors concluded that there was a Debye salt effect which increased greatly the ionic dissociation of the acid. However, the ionic strengths of these solutions, as evidenced by their extremely low conductances, are so small that such an interpretation would hardly seem valid.

between other molecules because of its own tendency to form hydrogen bonds with them. Carboxylic acids, for example, do not associate into dimers in dioxane. Consequently, a complex anion of the type postulated above would hardly be expected to be sufficiently stable in dioxane to give the observed maxima in the titration curves, unless an exceptionally stable structure resulted. Although the presence of a negative charge on the complex ion should tend to strengthen this conventional type of hydrogen bonding, it would appear more likely that the ion has a somewhat different structure. Resonance in the carboxylate ion gives both carbon-oxygen bonds a partial double bond character and makes them equivalent. In the complex anion the proton of the second carboxyl group could assume a position where it was equally shared by all four oxygen atoms as indicated by the structure



Rather than the planar configuration shown, the four oxygens would, in all probability, be located tetrahedrally around the proton. Because of the compact structure and the gain in energy through complete resonance of both carboxyl groups, this configuration should be more stable than the previous structure involving the more conventional type of hydrogen bond.

The similarity in behavior of trichloroacetic acid and camphorsulfonic acid indicates a corresponding interaction between the latter acid and its salt. A bonding of the sulfonic acid group with the sulfonate ion in a manner analogous to that formulated in the case of the carboxylic acid would appear likely.

The behavior of the titrations involving picric acid and triethylamine in dioxane, where solutions containing both salt and base have unexpectedly high conductances, suggests a strong reaction between salt and base leading to the formation of a hydrogen-bonded complex cation, as $R_3N^+-H \ldots NR_3$ in this particular case. The possibility of forming this same complex cation exists in other cases, for example, in the titrations of trichloroacetic acid or camphorsulfonic acid with triethylamine in dioxane. Its actual existence to any significant extent is ruled out by the experimental data which fail to show any marked rise in conductance during the forward titrations after the equivalence point has been reached. This fact is not too surprising as the salts exist almost entirely in the form of ion pairs so that the behavior of the cation is influenced by the nature of the attached anion.

The anomalous behavior of titrations with picric acid and triethylamine in benzene has been discussed previously. In a few of the other titrations, small variations in conductance with time took place which were not confined to any particular portion of the titration curves. Since a direct current bridge was employed, it is quite possible that these variations were associated with some polarization phenomenon and could be eliminated by an alternating current method. These drifts were sometimes toward lower and sometimes toward higher conductances. In the titrations with picric acid and di-*n*-butylamine in benzene, for example, drifts toward lower conductance, or higher resistance, were noted. The conductance immediately after addition of the titrating solution and mixing was several percent higher than the steady value reached in 10 or 15 seconds. Reversal of the polarity of the bridge caused an immediate increase in conductance to or slightly above the initially observed value which was then followed by a decrease to the same steady value as before. Subsequent mixing also tended to restore the original value. A rather detailed study of an apparently analogous effect also with direct current, has been reported by Fuoss and Elliott [8] in which the electrolyte was tri-*n*-butylammonium picrate and the solvent, tricresyl phosphate, a highly viscous medium with a relatively low dielectric constant. The attainment of a steady state required a much longer time and the change in conductance was much greater in this case. These authors attributed this slow increase in effective resistance of the development of a space charge in the solution near the electrodes which deceased the potential gradient across the main body of the solution.

Drifts toward higher conductances, observed for example in titrations with trichloroacetic acid and *n*-heptylamine in dioxane, occurred more slowly and several minutes were required to reach a steady state. As before, mixing the solution restored the initial value. This drift cannot be attributed to the development of a space charge.

On reversal of the polarity, however, an effect similar to that described in connection with the titrations involving picric acid and di-*n*-butylamine was also observed, so that there would appear to be a superposition of at least two different effects. Observation of these drifts was more or less incidental since they did not interfere with the titrations, provided a consistent procedure was followed in taking the readings. Where the drifts were relatively slow, the initial conductances, reproducible on repeated mixing, were used. The final or steady values were used where the drift was quite rapid. In a majority of cases the systems were quite stable and no variation in conductance was observed either on reversal of the polarity or on mixing. Where drifts were observed, addition of the small amount of alcohol to the solvent eliminated them. To explain these drifts in certain systems and their absence in others will require a more thorough investigation employing both alternating and direct current methods.

The results of the present investigation show that conductimetric titrations of acids and bases are feasible in solvents of the lowest dielectric constants even though the conductances are lower by a factor of 10^{-8} than they would be in water. The diversified behavior of these systems, not anticipated from studies in the usual solvents, makes generalizations difficult. Qualitatively, the assumption of the formation of a complexion accounts for the behavior of a number of the titrations, but additional experimental data will be required before a more complete interpretation in terms of reaction equilibria can be made. The data also are of interest in connection with the general problem of acid-base equilibria in media of low dielectric constant. While in certain instances such reactions do seem to follow a simple mass law [9], in others the behavior is more complicated [10]. In addition to factors such as association of the acids and salts, the formation of complex salts as suggested by the present studies may introduce additional complications, particularly in cases where carboxylic or sulfonic acids are employed.

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Analyses of Alkylates and Hydrocodimers[1*]

By Augustus R. Glasgow, Jr., Anton J. Streiff,[2] Charles B. Willingham, and Frederick D. Rossini

This paper presents the results of work by the American Petroleum Institute Research Project 6 on the analyses, with respect to individual hydrocarbon components, of 28 different alkylates and hydrocodimers. The samples reported include 15 sulfuric-acid alkylates (one C_3, six C_4, one C_4-C_5, four C_5, one hot-acid dimer, one hot-acid trimer, and one cold-acid trimer), five hydrofluoric-acid alkylates (one C_3, one C_3-C_4, one C_4, one C_4-C_5, and one C_5), and 8 hydrocodimers. The analyses were made utilizing analytical distillations performed at high efficiency with high reflux ratio, together with accurately measured values of boiling point (obtained during the distillation) and of refractive index of the fractions of distillate.

Also included in this report is a summary of the results of the subsequent spectrographic analyses, with respect to individual components, of one of the C_4 alkylates by six different laboratories, involving one Raman, one mass, and four infrared spectrometers.

I. Introduction

As part of its war research program, the American Petroleum Institute Research Project 6 at the National Bureau of Standards was called upon, by the Technical Advisory Committee of the Petroleum Industry War Council and the National Advisory Committee for Aeronautics, to determine the hydrocarbon components in a number of representative alkylates and hydrocodimers.[3]

This report presents the results of the analyses, with respect to individual hydrocarbon components, of 28 different alkylates and hydrocodimers, including samples of sulfuric-acid alkylates, hydrofluoric-acid alkylates, sulfuric-acid hydrocodimers, and phosphoric-acid hydrocodimers.

The correlation of the composition of these alkylates and hydrocodimers with the conditions of manufacture on the one hand, and with the properties of the product on the other, is made in another report by Gould and Field [1].[4]

II. Samples Analyzed

The 28 different alkylates and hydrocodimers for which analyses are given in this report are listed in table 1,[5] which gives the API Research Project 6 sample number, the name of the sample, the maker of the material, and the date on which the original report of analysis of the material was issued. Additional identification and properties of the samples, the character of the "feed" stocks, etc. are given in the paper by Gould and Field [1].[5]

III. Procedure

The analyses were made by performing extended analytical distillations at high efficiency with high reflux ratio and utilizing accurately measured values of boiling points (to ± 0.01 deg C), obtained

*Presented at the annual meeting of the American Petroleum Institute, before the Division of Refining, at Chicago, Illinois, November 12, 1946.

[1] This investigation was performed at the National Bureau of Standards as part of the work of the American Petroleum Institute Research Project 6 on the Analysis, Purification, and Properties of Hydrocarbons.

[2] Research Associate on the American Petroleum Institute Research Project 6 at the National Bureau of Standards.

[3] In this report, the term "alkylate" is used, in conformity with industrial practice, to designate those mixtures of branched-chain paraffin hydrocarbons produced by the addition of olefins to paraffins. In particular, a propylene (or C_3) alkylate is one produced from materials that are largely propylene in the olefin stock and largely butanes in the paraffin stock; a butene (or C_4) alkylate is one produced from materials that are largely butenes in the olefin stock and butanes in the paraffin stock; a pentene (or C_5) alkylate is one produced from materials that are largely pentenes in the olefin stock and butanes in the paraffin stock; a dimer alkylate is one produced from materials that are largely octenes in the olefin stock and butanes in the paraffin stock; and a trimer alkylate is one produced from materials that are largely dodecenes in the olefin stock and butanes in the paraffin stock. Similarly, in conformity with industrial paractice, the term "hydrocodimer" is used to designate those mixtures of branched-chain paraffin hydrocarbons (largely octanes) produced by the hydrogenation of a "codimer" (largely octenes) that has been produced by the codimerization of butenes.

[4] Figures in brackets indicate the literature references at the end of this paper.

[5] The tables and figures are at the end of this paper.

during the distillations, and values of refractive index (to ± 0.0001) obtained on the fractions of distillate after the distillation.

Complete details of the assembly, testing, and operation of the distilling columns used in this work are given in another report [2].

The procedure followed in the analyses of the alkylates and hydrocodimers reported here may be simply illustrated by following through one of the samples, as follows:

A volume of 5,500 ml of a C_4 Alkylate (H_2SO_4), sample 27, was placed in still 4 on April 3, 1944. The distillation was continued until May 18, 1944, approximately 1,100 hr, with distillate being removed at the rate of 4.7 ml/hr. At each hour during the distillation (which corresponds to each 4.7 ml of distillate), the temperature of the liquid-vapor equilibrium in the head of the column was recorded to the nearest 0.01 deg C, and the increment in the volume of distillate was measured. The distillation yielded 272 fractions of distillate, each about 19 ml in volume.

The refractive index, n_D, at 25° C, of each of the fractions of distillate was measured [6] to ± 0.0001 with NBS Standard Sample of 2,2,4-trimethylpentane as a reference substance, on Valentine refractometers, Abbe type, graduated directly to 0.0001.

Plots of the boiling point, and of the refractive index of the fractions of distillate, as a function of the volume of distillate, were made on an expanded scale, with 1 mm on the horizontal scale equivalent to 5 ml in volume of the distillate, and with 1 mm on the vertical scale equivalent to 0.2 deg C in boiling point or to 0.0001 in refractive index. A reproduction of these plots for sample 27 is given in figure 19.

From its manner of preparation, the butene alkylate was known to be substantially all a mixture of paraffin hydrocarbons. The olefin content was checked by determining the bromine number, with pure, olefin-free "isooctane" as a reference.[7] The presence of possible small amounts of aromatic hydrocarbons, as well as olefin hydrocarbons, was checked by searching for abnormalities in the curve of refractive index versus volume, especially at or near the "break points". Where found in significant amount, allowance for the olefin or aromatic hydrocarbon was appropriately made in the reduction of the data from the curve of refractive index versus volume.

The next step in the reduction of the data was to determine the appropriate break points between adjoining horizontal or nearly horizontal parts of the curves of boiling point versus volume and refractive index versus volume. (For convenience, these parts of the distillation curve will be called "flats".)

The appropriate break point between two adjoining flats is that point at which the distillate has a composition that corresponds substantially to equal amounts of the material of the two flats. The break points can be determined easily in terms of equal volumes of material in the case of the curve of refractive index, and in terms of equimolal amounts in the case of the curve of boiling point. Actually, however, the difference between equal volumes and equimolal amounts is not significant in connection with the location of the break points in the present investigation.

In the simple case where each flat represents substantially one compound (as, for example, compound A in one flat and compound B in the succeeding flat), the appropriate break point in the curve of boiling point versus volume is at that volume where the distillate is, in mole fraction, 0.5 A and 0.5 B, which point is located as being at the temperature determined by the following relation:

$$0.5\ P_A + 0.5 P_B = P. \qquad (1)$$

In eq 1, P_A and P_B represent the vapor pressures of pure A and pure B, respectively, at the sought-for temperature t_M, and P is the total pressure at which the distillation is performed. This ideal relation holds sufficiently well for the mixtures of branched-chain paraffin hydrocarbons encountered in this investigation. The sought-for temperature, t_M, will always be less than the average of t_A and t_B. The difference between t_M and the average of t_A and t_B becomes insignificant as t_B approaches t_A, and, when t_A and t_B differ only by a few degrees, the break point may be located midway in temperature between the two flats without significant error. The break point obtained for equimolal amounts is assumed to be the same as the break point for equal volumes, within the significance of the present data.

Whenever the material on either or both flats is

[6] Edith M. Pauls, laboratory assistant on the API Research Project 6 performed most of these measurements.

[7] The bromine numbers were determined under the supervision of R. C. Hardy, of the Bureau's Section on Lubricants and Liquid Fuels.

composed of two or more components, the break point is located as outlined above, except that the temperatures on each of the two flats are taken as measured and considered to be the average for the components on the given flats, and further, the changes of the boiling point with pressure are taken as an average of those for the possible components.

Actually, while the location of the temperature of the break point becomes less certain, the greater the difference in temperature between the two flats, the uncertainty of the location of the break point in terms of volume of distillate is little affected because of the fact that, as the difference in the two temperatures increases, the break between the two flats becomes sharper and there is a much more rapid change of temperature with volume.

For the curve of refractive index versus volume, when two adjoining flats represent single components, A and B, respectively, the break point is located at that point at which, when a vertical line is erected, the area bounded by the vertical line, the refractive index curve to the left of the vertical line, and a horizontal extension (to the right) of the refractive index flat for compound A, is equal to the area bounded by the vertical line, the refractive index curve to the right of the vertical line, and a horizontal extension (to the left) of the refractive index flat for compound B. This procedure assumes the refractive indices to be additive with volume on mixing, which assumption will not introduce any significant error for the mixtures of paraffin hydrocarbons encountered in this investigation.

When one or both of the flats represent two or more components, the same procedure is followed, with the understanding that the refractive index flat represents the mean refractive index for the two or more components in each case.

If the data are exact and have been correctly reduced, the break points on the curve of boiling point versus volume will be located at the same volume as the break point on the curve of refractive index versus volume, within their respective limits of uncertainty. (In the present investigation, appropriate correction was made, as necessary, for the volume of liquid hold-up in the line between the thermometer and the receiver, in order to have the values of boiling point and refractive index apply exactly to the same part of the distillate.

The next step was to estimate the relative amounts of the individual components when two or three resolvable compounds occur in one flat. When there are only two possible components in one flat, the relative amounts of the two components can be calculated from the mean value of the boiling point on the flat and the known values of the boiling points of the two pure compounds (at the given pressure), according to relations

$$x_C+x_D=1 \tag{2}$$

and

$$x_CP_C+x_DP_D=P_M, \tag{3}$$

where x_C and x_D are the mole fractions of the two components C and D, and P_C, P_D, and P_M are the vapor pressures, respectively, of pure C, pure D, and the mixture at the given temperature, t. An independent value for the relative amounts of the two components can likewise be calculated from the mean value of the refractive index on the flat and the known values of the refractive indices of the two pure compounds, according to eq 2 and the relation

$$x_Cn_C+x_Dn_D=n_M, \tag{4}$$

where n_C, n_D, and n_M are the refractive indices, respectively, of pure C, pure D, and the mixture. These two values of the relative amounts should be in accord within their respective limits of uncertainty.[6] However, when P_C is nearly equal to P_B, and n_C is nearly equal to n_D, the relative amounts of the two compounds cannot be determined from these properties.

When a given flat represents three components, A, B, and C, the relative amounts of the three components may be estimated from the following three simultaneous equations:

$$x_A+x_B+x_C=1 \tag{5}$$

$$n_M=x_An_A+x_Bn_B+x_Cn_C \tag{6}$$

$$P_M=x_AP_A+x_BP_B+x_CP_C. \tag{7}$$

[6] The uncertainty in the value of the relative amounts of the two components in one flat determined from the curve of refractive index versus volume is given by the relation

$$\sigma x_C=[1/(n_D-n_C)]\,[x_C^2\sigma^2n_A+x_D^2\,\sigma^2n_D+\sigma^2n_M]^{1/2},$$

In this equation, n_D-n_C is the difference in the refractive indices of pure C and pure D, x_C is the mole fraction of the material which is component C, x_D (or $1-x_C$) is the mole fraction of the material which is component D, and σn_C, σn_D, and σn_M are the uncertainties in the values of refractive indices of pure C, pure D, and the mixture, respectively.

The corresponding uncertainty for the case of the curve of boiling point versus volume is obtained by substituting vapor pressure or temperature for refractive index in the foregoing equation.

In these equations, x_A, x_B, and x_C are the fractions of A, B, and C, respectively; n_A, n_B, n_C, and n_M are the refractive indices of A, B, C, and the mixture, respectively; and P_A, P_B, P_C, and P_M are the vapor pressures of A, B, C, and the mixture, respectively, at the temperature on the flat. Whenever the value of a given property is nearly the same for two of the components, it will not be possible to determine the relative amounts of these two components, but only their sum, from the above relations.

When a given flat represents more than three components, it is not possible to calculate the amounts of the individual components without measuring an additional property which has sufficiently different values for the several components.

In the case of minor components appearing near the beginning or the end of one of the flats in the curve of boiling point versus volume, the amount of such components can be calculated from the curve of refractive index versus volume when these minor components differ sufficiently in refractive index from the main component of the given flat.

The values of refractive indices, and of boiling points at various pressures, for the pure paraffin hydrocarbons involved in this investigation were taken from the tables of the API Research Project 44 [3].

Following the above procedure, and referring to the curves of boiling point versus volume and refractive index versus volume in figure 19, the various components of the butene alkylate analyzed as sample 27 were determined as follows:

(1) From flats with one component: Material (largely *n*-butane) lower-boiling than isopentane; isopentane; *n*-pentane; 2,3-dimethylbutane; 2,2,4-trimethylpentane; 2,3,4-trimethylpentane; 2,2,5-trimethylhexane; 2,3,5-trimethylhexane.

(2) From flats with one major component, with one or more minor components at the beginning or end of the flat: 2-Methylpentane; 2,4-dimethylpentane; 2,3-dimethylpentane; 2,3,3-trimethylpentane.

(3) From flats with two major components, with one or two minor components at the beginning or end of the flat: 2,5-dimethylhexane plus 2,4-dimethylhexane.

(4) As minor components occurring at the beginning or end of a flat: 3-Methylpentane; 2,2-dimethylpentane; 2,2,3-trimethylbutane; 2-methylhexane; 3-methylhexane; 2,2-dimethylhexane; 2,2,3-trimethylpentane; 2,3-dimethylhexane; 3,4-dimethylhexane.

Table 2 summarizes the important details concerning the analytical distillation of each of the 28 samples.

IV. Analyses of 28 Alkylates and Hydrocodimers

Figures 1 to 28, inclusive, show graphically the results of the analytical distillations of the 28 samples listed in table 1. These illustrations show, as a function of the volume of distillate, and of the percentage by volume of distillate, the boiling point of the distillate and its refractive index. Table 2 gives some additional information concerning the analytical distillation of the 28 samples.

Tables 3 to 7 give the composition, with respect to individual components, of the material above pentanes, for each of the 28 samples, as follows: Table 3, two propylene alkylates and one mixed propylene-butene alkylate; table 4, seven butene alkylates; table 5, five pentene alkylates and two mixed butene-pentene alkylates; table 6, one "dimer" alkylate and two "trimer" alkylates; table 7, eight hydrocodimers.

The butene alkylate analyzed by the API Research Project 6 as sample 24 was also analyzed in part by several other laboratories. Table 8 gives a comparison of the analysis of this butene alkylate by the following laboratories: API Research Project 6, by the method described in this report; Standard Oil Co. (Indiana), by analytical distillation and physical properties of the distillate; Shell Oil Co., by analytical distillation and physical properties of distillate, plus infrared for 2,3,4-trimethylpentane and 2,3,3-trimethylpentane.

The values given in tables 9 to 13 have been calculated from the values given in tables 3 to 7. For the 20 alkylates and 8 hydrocodimers, table 9 gives the relative amounts of hexanes, heptanes, octanes, and nonanes, and higher paraffins. Tables 10, 11, 12, and 13 give, for the 28 samples, the relative amounts of some individual branched-chain hexanes, heptanes, octanes, and nonanes, respectively.

V. Results of Cooperative Spectrographic Analysis of an Alkylate

In order to obtain comparative data on the ectrographic analysis of a representative alky- te with the spectrometers then being brought to use by the laboratories of the petroleum dustry, and also to see how such analyses might mpare with analyses made by the method of tended analytical distillation (plus boiling point d refractive index) as described in this report, e of the alkylates analyzed in the present work s prepared for subsequent spectrographic anal- s by several different laboratories.

The alkylate selected for this cooperative analy- was the butene alkylate analyzed as sample 27. e approximately 5 liters of distillate, collected 272 fractions, was blended into 50 lots, as shown the horizontal row of numbers near the middle figure 19. From each of these 50 lots, 8 sam- s of 4 ml each were sealed in glass ampoules. e material remaining in each of the 50 lots s also sealed in glass ampoules for retaining. e set of 50 samples was sent to each of the boratories for spectographic analysis. The labo- tories participating in the cooperative specto- aphic analysis of sample 27, together with the thods used, and the date of reporting the analy- , are as follows: Standard Oil Development ., Elizabeth, N. J.; with infrared spectrometer; alysis reported January 2, 1945. Atlantic Re- ing Co., Philadelphia, Pa.; with mass spectrom- r; analysis reported June 22, 1945. Socony- cuum Laboratories, Paulesboro, N. J.; with frared spectrometer; analysis reported July 25, 45. Sun Oil Co., Norwood, Pa.; with Raman ctrometer; analysis reported October 8, 1945. niversal Oil Products Co., Riverside, Ill.; with frared spectrometer; analysis reported April 24, 46. Phillips Petroleum Co., Bartlesville, Okla.; th infrared spectrometer; analysis reported ne 20, 1946.

The spectrographic analyses reported by the veral cooperating laboratories are summarized table 14. The results indicate good agreement t only among the laboratories using the same pe of spectrometer (infrared), but also among se using different types of spectrometers (mass, man, infrared). Further, the results from the ctrographic analyses are in good accord with analysis of sample 27 from the present work.

VI. Discussion

In connection with the analyses presented in this report, the following observations may be made:

In relative amount among the heptanes, octanes, and nonanes, the heptanes are largest in the propylene alkylates, the nonanes are largest in the pentene alkylates, and the octanes are largest in the butene alkylates and the dimer and trimer alkylates.

The various paraffin hydrocarbon isomers are produced in relative amounts that do not, in a broad sense, correspond to thermodynamic equilibrium, although in some cases, two or three isomers of not too dissimilar structure may be found in relative amounts corresponding approximately to thermodynamic equilibrium [4, 5]. This observation is apparent from the fact that the relative amounts of the individual dimethylhexanes and the individual trimethylpentanes can be appreciably altered by changes in the conditions of manufacture, as shown in the report by Gould and Field [1].

In the 15 alkylates having appreciable amounts of hexanes, the amount of 2,3-dimethylbutane was, on the average, 64 ± 10 percent of the total hexanes.

In both the alkylates and hydrocodimers, the heptanes present in large relative amount are 2,4-dimethylpentane and 2,3-dimethylpentane, with 2,2-dimethylpentane, 2-methylhexane, and 3-methylhexane in small amount, and the other heptanes being substantially absent.

In the alkylates, the octanes present in large relative amount are 2,2,4-trimethylpentane, 2,3,4-trimethylpentane, and 2,3,3-trimethylpentane, with 2,5-dimethylhexane, 2,4-dimethylhexane, and 2,3-dimethylhexane in small amount and the other octanes being substantially absent.

In the hydrocodimers, excluding the hot-acid hydrocodimer, sample 35, the octane present in largest relative amount is 2,3,4-trimethylpentane, with 2,2,4-trimethylpentane, 2,2,3-trimethylpentane, and 2,3,3-trimethylpentane in smaller amount, 2,2-dimethylhexane, 2,5-dimethylhexane, 2,4-dimethylhexane, 2,3-dimethylhexane, and 3,4-dimethylhexane in still smaller amount, and the other octanes substantially absent.

In the 11 alkylates having appreciable amounts of nonanes, the relative amounts of the two

trimethylhexanes present in large amount were substantially constant, being 82.9 ±1.5 for 2,2,5-trimethylhexane and 17.1 ±1.5 for 2,3,5-trimethylhexane.

The hydrocodimers, excluding the hot-acid hydrocodimer, sample 35, differ from the alkylates in usually having in relative amount, among the octanes, less 2,2,4-trimethylpentane, more 2,2-dimethylhexane, more 2,2,3-trimethylpentane, more 2,3,4-trimethylpentane, less 2,3,3-trimethylpentane, and more 3,4-dimethylhexane, and in relative amount among the heptanes, more 2,3-dimethylpentane and less 2,4-dimethylpentane.

The dimer and trimer alkylates, for the production of which [1] the olefin charging stocks were largely C_8 and C_{12} olefins, respectively, have compositions that are not greatly different from the regular butene alkylates.

Eight different highly branched paraffin hydrocarbons can be obtained, in a purity of about 90 mole percent or better, by efficient distillation (equivalent to 100 or more theoretical plates) of appropriate alkylates or hydrocodimers, as follows: 2,4-Dimethylpentane from C_8 alkylate; 2,3-dimethylpentane from C_8 alkylate; 2,2,4-trimethylpentane from C_8 alkylate; 2,2,3-trimethylpentane from hydrocodimer (hot-acid); 2,3,4-trimethylpentane from hydrocodimer (phosphoric acid); 2,3,3-trimethylpentane from C_8 alkylate; 2,2,5-trimethylhexane from C_9 alkylate; 2,3,5-trimethylhexane from C_9 alkylate.

Grateful acknowledgement is made to the Standard Oil Co. (Ind.), Shell Oil Co., Standard Oil Development Co., Atlantic Refining Co., Socony-Vacuum Laboratories, Sun Oil Co., Universal Oil Products Co., and the Phillips Petroleum Co. for permission to include in this report the results of analyses made by their respective laboratories, as indicated in sections IV and V of this report.

VII. References

[1] D. W. Gould and H. W. Field, Proc. Am. Petroleum Inst. **27** (III), (1946).

[2] C. B. Willingham and F. D. Rossini, J. Research NBS **37,** 15 (1946) RP1724.

[3] American Petroleum Institute Research Project 44 at the National Bureau of Standards. Tables 1a, 2a, 3a, 4a. Boiling point, dt/dP, refractive index, density, and freezing point.

[4] F. D. Rossini, E. J. Prosen, and K. S. Pitzer, J. Research NBS **27,** 529 (1941) RP1440.

[5] E. J. Prosen, K. S. Pitzer, and F. D. Rossini, J. Research NBS **34,** 255 (1945) RP1641.

TABLE 1.—*List of the 28 alkylates and hydrocodimers*

API Research Project 6 sample No.	Sample	Maker of the sample	Date of report of analysis
1	C_4 Alkylate (H_2SO_4)	Standard Oil Co. of New Jersey.	Oct. 31, 1942
2	do	Texas Co	Nov. 10, 1942
4	Hydrocodimer (solid phosphoric acid).	Standard Oil Co (Indiana).	Dec. 19, 1942
7	C_3 alkylate (H_2SO_4)	Standard Oil Co. of New Jersey.	May 22, 1943
9	C_4 Alkylate (H_2SO_4)	Atlantic Refining Co.	Nov. 30, 1943
10	do	do	Dec. 18, 1943
11	C_7-C_8 alkylate (H_2SO_4).	do	Dec. 11, 1943
12	C_3 alkylate (H_2SO_4)	do	Dec. 6, 1943
13	C_4 alkylate (HF)	Sinclair Refining Co.	Nov. 30, 1943
14	C_3 alkylate (HF)	do	Dec. 6, 1943
15	C_7-C_8 alkylate (HF)	do	Dec. 18, 1943
16	C_7-C_8 alkylate (HF)	do	Apr. 29, 1944
17	C_3 alkylate (HF)	do	Dec. 11, 1943
20	C_3 alkylate (H_2SO_4)	Shell Oil Co	Apr. 22, 1944
21	Trimer (hot acid) alkylate (H_2SO_4).	do	May 6, 1944
22	C_3 alkylate (H_2SO_4)	do	May 13, 1944
23	do	do	May 20, 1944
24	C_4 alkylate (H_2SO_4)	Standard Oil Co. of Ohio.	Nov. 30, 1943
27	do	Standard Oil Co. of New Jersey, Louisiana Division.	Oct. 15, 1944
33	Hydrocodimer (phosphoric acid).	Standard Oil Co. of New Jersey.	Oct. 31, 1944
34	Dimer (hot acid) alkylate (H_2SO_4).	Shell Oil Co	Oct. 15, 1944
35	Hydrocodimer (hot-acid).	do	Jan. 31, 1945
36	Hydrocodimer (Lawrenceville).	Texas Co	May 15, 1945
37	Hydrocodimer (Tulsa).	do	May 31, 1945
41	Hydrocodimer (Lima 6).	Standard Oil Co. of Ohio.	June 15, 1945
42	Hydrocodimer (Lima 7).	do	Sept. 15, 1945
43	Trimer (cold acid) alkylate (H_2SO_4).	Pure Oil Co	June 15, 1945
44	Hydrocodimer (HSO-1684).	Trimpell, Ltd.	June 30, 1945

Table 2 – Information on the analytical distillation of 20 alkylates and 8 hydrocodimers.

Sample No.	Material	Distillation								Analysis given in table
		Distilling column number[a]	Number of theoretical plates (approx.)[a]	Reflux ratio (approx.)	Rate of collection of distillate	Volume of charge	Volume of each fraction	Total time of distillation	Results plotted in figure	
					ml/hour	ml	ml	hours		
1	C_6 Alkylate (H_2SO_4)	H	110	120/1	5	2600	15	510	1	4
2	C_4 Alkylate (H_2SO_4)	H	110	120/1	5	2590	15	510	2	4
4	Hydrocodimer (solid phosphoric acid)	H	110	120/1	5	2600	15	575	3	7
7	C_5 Alkylate (H_2SO_4)	H	110	120/1	5	2600	15	530	4	5
9	C_4 Alkylate (H_2SO_4)	H	110	120/1	5	2600	15	600	5	4
10	C_4 Alkylate (H_2SO_4)	H	110	120/1	5	2600	15	550	6	4
11	C_4–C_5 Alkylate (H_2SO_4)	H	110	120/1	5	2600	15	600	7	5
12	C_5 Alkylate (H_2SO_4)	H	110	120/1	5	2595	15	575	8	5
13	C_4 Alkylate (HF)	H	110	120/1	5	2600	15	575	9	4
14	C_5 Alkylate (HF)	H	110	120/1	5	2565	15	530	10	5
15	C_4–C_5 Alkylate (HF)	Q	100	120/1	2.5	1600	7.5	695	11	5
16	C_3–C_4 Alkylate (HF)	Z	100	120/1	2.5	1790	7.5	670	12	3
17	C_3 Alkylate (HF)	P	100	120/1	2.5	1625	7.5	620	13	3
20	C_3 Alkylate (H_2SO_4)	Z	100	120/1	2.5	1800	7.5	670	14	3
21	Trimer (hot acid) Alkylate (H_2SO_4)	3	100	120/1	2.5	1760	7.5	740	15	6
22	C_5 Alkylate (H_2SO_4)	2	100	120/1	2.5	1790	7.5	740	16	5
23	C_5 Alkylate (H_2SO_4)	3	100	120/1	2.5	1790	7.5	790	17	5
24	C_4 Alkylate (H_2SO_4)	P	100	120/1	2.5	1600	7.5	620	18	4
27	C_6 Alkylate (H_2SO_4)	4	200	150/1	4.7	5500	19	1100	19	4
33	Hydrocodimer (phosphoric acid)	2	100	120/1	2.5	1800	7.5	740	20	7
34	Dimer (hot acid) Alkylate (H_2SO_4)	2	100	120/1	2.5	2000	7.5	770	21	6
35	Hydrocodimer (hot acid)	3	100	120/1	2.5	1800	7.5	700	22	7
36	Hydrocodimer (Lawrenceville)	3	100	120/1	2.5	2000	7.5	860	23	7
37	Hydrocodimer (Tulsa)	2	100	120/1	2.5	2000	7.5	990	24	7
41	Hydrocodimer (Lima 6)	2	100	120/1	2.5	2000	7.5	890	25	7
42	Hydrocodimer (Lima 7)	2	100	130/1	2.3	2000	9.2	910	26	7
43	Trimer (cold acid) Alkylate (H_2SO_4)	2	100	130/1	2.3	1970	9.2	890	27	6
44	Hydrocodimer (H30–1684)	3	100	130/1	2.3	2370	9.2	1100	28	7

[a] See reference 2. Column H was the same as column 9 except that the length of the rectifying section was 2.71 meters (107 inches). Columns P and Q were similar to columns 2 and 3.

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Table 3 – Analyses of two propylene alkylates and one mixed propylene-butene alkylate

Components	Boiling point at 1 atm. °C	C_3 Alkylate (H_2SO_4) Sample 20 (see figure 15)	C_3 Alkylate (HF) Sample 17 (see figure 14)	C_3–C_4 Alkylate (HF) Sample 16 (see figure 13)
		Percentage by volume (above pentanes)		
2,3-Dimethylbutane	58.0	3.5[a] ± 1.0	2.9[a] ± 0.6	1.4[a] ± 0.7
2-Methylpentane	60.3	1.7 ± 0.9 } 5.3 ± 1.0	1.4 ± 0.5 } 5.0 ± 0.5	0.9 ± 0.5 } 2.3 ± 0.5
3-Methylpentane	63.3	0.1 ± 0.1	0.7 ± 0.4	
2,2-Dimethylpentane	79.2	1.1 ± 1.1	0.8 ± 0.8	0.7 ± 0.7
2,4-Dimethylpentane	80.5	26.2[b] ± 1.5 } 27.3 ± 0.5	18.2[b] ± 0.8 } 19.0 ± 0.5	4.2[b] ± 1.0 } 4.9 ± 0.5
2,3-Dimethylpentane	89.8	36.1 ± 1.1	21.1 ± 1.0	4.5 ± 1.0
2-Methylhexane	90.1	} 38.4 ± 0.5	} 22.4 ± 0.5	} 5.3 ± 0.8
3-Methylhexane	92.0	2.3 ± 1.1	1.3 ± 1.0	0.8 ± 0.5
2,2,4-Trimethylpentane	99.2	7.8 ± 0.5	16.3 ± 0.5 } 16.5 ± 0.5	30.04 ± 1.0
Olefins	99–109		0.2 ± 0.1	
Toluene	110.6			0.06 ± 0.02
2,5-Dimethylhexane	109.1	} 2.5[c] ± 0.8 } 3.3 ± 0.8	} 4.0[c] ± 1.0 } 5.1 ± 1.0	} 9.1[c] ± 2.0 } 11.4 ± 1.2
2,4-Dimethylhexane	109.4			
2,2,3-Trimethylpentane	109.8	0.8 ± 0.5	1.1 ± 0.6	2.3 ± 1.2
2,3,4-Trimethylpentane	113.5	2.5 ± 1.0	3.4 ± 1.5	6.8 ± 2.0
2,3,3-Trimethylpentane	114.8	3.2 ± 1.0 } 6.9 ± 1.0	3.9 ± 1.5 } 8.2 ± 1.5	6.7 ± 2.0 } 17.5 ± 2.0
2,3-Dimethylhexane	115.6	1.2[d] ± 0.6	0.9[d] ± 0.5	4.0[d] ± 2.0
Isoparaffins	115.6–124.1			1.3 ± 0.7
2,2,5-Trimethylhexane	124.1	1.4 ± 0.7	4.5 ± 1.5	8.2 ± 1.5
Isononanes	126–143	0.8 ± 0.5	2.4 ± 0.5	
2,3,5-Trimethylhexane	131.4			1.83 ± 1.0 } 1.9 ± 1.0
Aromatics	125–133			0.07 ± 0.04
Isononanes	133–143			1.53 ± 0.9 } 1.6 ± 0.9
Aromatics	133–149			0.07 ± 0.04
Isoparaffins	143–151	2.2 ± 1.0	3.3 ± 1.0	
Isoparaffins	>143			15.5 ± 0.9
Isoparaffins	151–160	1.5 ± 0.7	2.2 ± 0.8	
Isoparaffins	>160	5.1 ± 0.8		
Isoparaffins	160–175		7.7 ± 1.5	
Isoparaffins	>175		3.7 ± 1.0	
Total		100.0	100.0	100.0

[a] May include a small amount of 2,2-dimethylbutane.
[b] May include a small amount of 2,3-trimethylbutane.
[c] May include a small amount of 2,2-dimethylhexane.
[d] May include a small amount of 3,4-dimethylhexane.

Table 4 – Analyses of seven butene alkylates

Components	Boiling point at 1 atm.	C_4 Alkylate (H_2SO_4) Sample 1 (see figure 1)	C_4 Alkylate (H_2SO_4) Sample 2 (see figure 2)	C_4 Alkylate (H_2SO_4) Sample 9 (see figure 5)	C_4 Alkylate (H_2SO_4) Sample 10 (see figure 6)	C_4 Alkylate (H_2SO_4) Sample 24 (see figure 18)	C_4 Alkylate (H_2SO_4) Sample 27 (see figure 19)	C_4 Alkylate (HF) Sample 13 (see figure 9)
	°C	Percentage by volume (above pentanes)						
2,2-Dimethylbutane	49.7	0.6 ± 0.4	0.5[b] ± 0.03	6.5[a] ± 0.5	7.0[a] ± 0.9	2.1[a] ± 0.5	5.2[a] ± 0.9	2.1[a] ± 0.5
2,3-Dimethylbutane	58.0	5.5 ± 1.0	8.1 ± 0.6	1.8 ± 0.5	2.4 ± 0.9		1.2 ± 0.6	
2-Methylpentane	60.3	1.8 ± 0.8	3.2 ± 0.6	8.3 ± 0.5	9.4 ± 0.5		0.4 ± 0.2	
3-Methylpentane	63.3	0.9 ± 0.6	0.7 ± 0.5				6.8 ± 0.5	
		8.8 ± 0.5	12.5[b] ± 0.5					
2,2-Dimethylpentane	79.2		0.7 ± 0.4	0.5 ± 0.3	0.8 ± 0.5		0.2 ± 0.2	
2,4-Dimethylpentane	80.5	3.6[b] ± 0.5	5.5[c] ± 0.5	4.2[c] ± 1.0	3.9[c] ± 1.0	1.1[c] ± 0.5	3.7 ± 1.0	2.6[c] ± 0.5
2,2,3-Trimethylbutane	80.9		6.2 ± 0.5	4.7 ± 1.0	4.7 ± 1.0		0.2 ± 0.2	
							4.1 ± 0.5	
2,3-Dimethylpentane	89.8	2.2 ± 1.1	3.4 ± 0.8	2.1 ± 0.5	2.5 ± 0.5		2.6 ± 0.7	
2-Methylhexane	90.1	0.9 ± 0.5	1.7 ± 0.8	0.7 ± 0.4	0.5 ± 0.3	1.0 ± 0.5	0.3 ± 0.2	1.9 ± 0.5
3-Methylhexane	92.0	3.1 ± 0.5	5.1 ± 0.6	2.8 ± 0.5	3.0 ± 0.5		2.9 ± 0.5	
2,2,4-Trimethylpentane	99.2	30.1 ± 0.6	22.4 ± 0.6	25.9 ± 0.5	26.8 ± 0.5	35.5 ± 0.5	26.7 ± 1.0	41.7 ± 0.5
"Unsaturated"	100-109		0.05 ± 0.03					
2,2-Dimethylhexane	106.8						0.3 ± 0.2	
2,5-Dimethylhexane	109.1	8.1[d] ± 1.2	10.3[d] ± 1.2	7.9[d] ± 1.0	8.3[d] ± 1.0	3.4[d] ± 1.0	7.2 ± 1.5	13.4[d] ± 1.2
2,4-Dimethylhexane	109.4	9.9 ± 1.0	12.2 ± 1.0	9.6 ± 1.0	9.9 ± 1.0	5.4 ± 1.0	8.8 ± 1.0	16.3 ± 1.1
2,2,3-Trimethylpentane	109.8	1.8 ± 0.8	1.9 ± 0.8	1.7 ± 1.0	1.6 ± 0.8	2.0 ± 1.0	1.3 ± 0.7	2.9 ± 1.2
2,3,4-Trimethylpentane	113.5	9.3 ± 1.2	15.3 ± 2.0	16.4 ± 2.0	19.2 ± 2.0	24.0 ± 2.0	14.3 ± 2.0	9.4 ± 2.0
2,3,3-Trimethylpentane	114.8	14.5 ± 1.2	10.4 ± 2.0	12.1 ± 2.0	14.9 ± 2.0	25.2 ± 2.0	13.5 ± 2.0	10.0 ± 2.0
2,3-Dimethylhexane	115.6	3.7[e] ± 1.2	3.4[e] ± 2.0	4.2[e] ± 1.5	2.3[e] ± 1.2	2.4[e] ± 1.5	3.3 ± 1.5	6.2[e] ± 2.0
3,4-Dimethylhexane	117.7	27.5 ± 1.5	29.1 ± 1.5	32.7 ± 1.5	36.4 ± 1.5	51.6 ± 1.5	0.4 ± 0.3	25.6 ± 1.5
							34.5 ± 1.5	
Isoparaffins	>115.6					3.3 ± 0.5		
2,2,5-Trimethylhexane	124.1	12.7 ± 0.8	8.8 ± 0.8	4.9 ± 1.0	6.3 ± 1.5		4.9 ± 1.0	3.4 ± 1.0
Isoparaffins	>124.1							6.4 ± 0.5
2,3,5-Trimethylhexane	131.4	1.9 ± 0.6	1.9 ± 0.6				1.0 ± 0.5	
Higher boiling material	>131.4	2.4 ± 0.5	1.7 ± 0.5					
Isoparaffins	126-142			2.3 ± 0.5	2.0 ± 0.7			
Isononanes	132-143						0.5 ± 0.3	
Isoparaffins	142-160			2.9 ± 0.5			2.5 ± 1.0	
Isoparaffins	>143				1.5 ± 0.5			
Isoparaffins	160-180			3.8 ± 1.0			3.0 ± 1.5	
Isoparaffins	>180			2.1 ± 1.0			7.3 ± 1.5	
Total		100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] May include a small amount of 2,2-dimethylbutane
[b] May include a small amount of 2,2-dimethylpentane
[c] May include a small amount of 2,2,3-trimethylbutane
[d] May include a small amount of 2,2-dimethylhexane
[e] May include a small amount of 3,4-dimethylhexane

Table 5 — Analyses of five pentene alkylates and two mixed butene-pentene alkylates

Components	Boiling point at 1 atm	C_5 Alkylate (H_2SO_4) Sample 7 (see figure 4)	C_5 Alkylate (H_2SO_4) Sample 12 (see figure 8)	C_5 Alkylate (H_2SO_4) Sample 22 (see figure 16)	C_5 Alkylate (H_2SO_4) Sample 23 (see figure 17)	C_5 Alkylate (HF) Sample 14 (see figure 14)	C_4-C_5 Alkylate (HF) Sample 15 (see figure 11)	C_4-C_5 Alkylate (HF) Sample 11 (see figure 7)
	°C	Percentage by volume (above pentanes)						
Cyclopentane	49.3		0.5 ± 0.3		0.5 ± 0.2			0.3 ± 0.1
2,2-Dimethylbutane	49.7		0.2 ± 0.1 } 0.7 ±0.4		0.1 ± 0.1 } 0.6 ±0.2			0.3 ± 0.2 } 0.6 ±0.3
2,3-Dimethylbutane	58.0	2.6[a] ± 0.8	2.7 ± 0.5		2.1 ± 0.8			2.8 ± 0.5
2-Methylpentane	60.3	2.1 ± 0.8	2.0 ± 0.5	3.2[a] ± 1.0	1.8 ± 0.9	1.6[a] ± 0.5	1.5[a] ± 0.5	1.4 ± 0.5
3-Methylpentane	63.3	1.1 ± 0.5	1.1 ± 0.5 } 5.8 ±0.5		0.4 ± 0.3 } 4.3 ±0.9			0.5 ± 0.2 } 4.7 ±0.5
Olefins	58-73	0.00± 0.005 } 5.8 ±0.5						
2,2-Dimethylpentane	79.2	1.8[b] ± 0.8	2.1[b] ± 0.5	1.5[b] ± 0.8	1.7[b] ± 0.5	1.4[b] ± 0.5	1.8[b] ± 0.5	2.3[b] ± 0.5
2,4-Dimethylpentane	80.5							
2,3-Dimethylpentane	89.8				1.0 ± 0.5			1.1 ± 0.5
2-Methylhexane	90.1	1.7 ± 0.8	1.7 ± 0.5	0.9 ± 0.5	0.5 ± 0.3 } 1.5 ±0.5	1.9 ± 0.5	1.7 ± 0.5	0.8 ± 0.4 } 1.9 ±0.5
3-Methylhexane	92.0							
2,2,4-Trimethylpentane	99.2	13.1 ± 0.8	12.4 ± 0.5	21.7 ± 1.0	17.2 ± 0.5	24.2 ± 0.5	33.3 ± 0.5	20.1 ± 0.5
Olefins	73-100	0.00± 0.005 } 13.1 ±0.8						
2,5-Dimethylhexane	109.1							
2,4-Dimethylhexane	109.4	4.3[c] ± 2.0	4.1[c] ± 1.0	3.7[c] ± 1.2	3.9[c] ± 1.0	3.9[c] ± 1.0	10.1[c] ± 1.0	5.3[c] ± 1.0
2,2,3-Trimethylpentane	109.8	0.9 ± 0.5 } 5.2 ±2.0	0.7 ± 0.5 } 4.8 ± 1.0	0.7 ± 0.4 } 4.4 ± 1.0	0.8 ± 0.5 } 4.7 ± 1.0	0.7 ± 0.4 } 4.6 ± 1.0	2.1 ± 1.0 } 12.2 ± 1.0	0.8 ± 0.5 } 6.1 ± 1.0
2,3,4-Trimethylpentane	113.5	6.6 ± 2.0	4.2 ± 2.0	9.4 ± 2.0	6.4 ± 1.5	5.4 ± 1.5	7.1 ± 1.5	11.6 ± 1.5
2,3,3-Trimethylpentane	114.8	4.5 ± 2.0	7.0 ± 2.0	9.5 ± 2.0	7.1 ± 1.5	4.2 ± 1.5	8.1 ± 1.5	10.2 ± 1.5
2,3-Dimethylhexane	115.6	1.1[d] ± 0.5	0.2[d] ± 0.2 } 11.4 ± 1.5	0.9[d] ± 0.5 } 19.8 ± 1.0	0.9[d] ± 0.4 } 14.4 ± 1.5	1.2[d] ± 0.6 } 10.8 ± 1.5	4.5[d] ± 2.0 } 19.7 ± 1.5	1.7[d] ± 0.8 } 23.5 ± 1.5
Olefins	112-125	0.04+ 0.02 } 12.2 ±2.5						
2,2,5-Trimethylhexane	124.1	34.2 ± 1.0	35.5 ± 2.0	29.5 ± 1.0	29.4 ± 1.5	29.3 ± 1.5	13.4 ± 1.5	24.0 ± 1.5
2,3,5-Trimethylhexane	131.4	6.6 ± 1.0	8.8 ± 2.0	6.5 ± 1.3	5.6 ± 1.8	5.5 ± 1.5	2.7 ± 1.0	5.8 ± 1.5
Isoparaffins	>131.4			12.5 ± 1.0				
Isononanes	132-144	4.4 ± 1.0	5.2 ± 1.0		5.2 ± 2.0	6.2 ± 1.0	4.7 ± 1.0	3.5 ± 0.8
Isoparaffins	144-151		5.6 ± 1.0		3.8 ± 1.5	2.9 ± 1.0	1.5 ± 0.5	3.0 ± 0.8
Isoparaffins	144-168	8.9 ± 1.0						
Olefins		0.05 ± 0.03 } 9.0 ± 1.0						
Isoparaffins	151-160		3.7 ± 0.5		2.2 ± 1.1	5.0 ± 1.0	1.2 ± 0.5	1.3 ± 0.5
Isoparaffins	>160		2.3 ± 0.5		9.4 ± 1.5	6.6 ± 1.0	6.3 ± 0.5	3.2 ± 0.5
Isoparaffins	168-189	3.1 ± 1.0						
Olefins		0.04± 0.02 } 3.1 ± 1.0						
Isoparaffins	>189	2.8 ± 0.5						
Olefins		0.05± 0.03 } 2.9 ±0.5						
Total		100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] May include small amount of 2,2-dimethylbutane.
[b] May include small amount of 2,2,3-trimethylbutane
[c] May include a small amount of 2,2-dimethylhexane.
[d] May include a small amount of 3,4-dimethylhexane.

Table 6-Analyses of three "dimer" and "trimer" alkylates

Components	Boiling point at 1 atm.	Dimer (hot acid) Alkylate (H_2SO_4) Sample 34 (see figure 21)		Trimer (hot acid) Alkylate (H_2SO_4) Sample 21 (see figure 15)		Trimer (cold acid) Alkylate (H_2SO_4) Sample 43 (see figure 27)	
	°C	Percentage by volume (above pentanes)					
2,3-Dimethylbutane	58.0	3.4[a] ± 0.9	4.9 ±0.5	4.2[a] ± 1.0	5.9 ±0.5	6.6[a] ± 0.8	8.4 ±0.6
2-Methylpentane	60.3	1.1 ± 0.5		1.7 ± 0.9		1.3 ± 0.7	
3-Methylpentane	63.3	0.4 ± 0.2				0.5 ± 0.3	
2,2-Dimethylpentane	79.2	0.3 ± 0.2	2.9 ±0.5	0.3 ± 0.3	4.9 ±0.5	0.5 ± 0.3	5.0 ±0.5
2,4-Dimethylpentane	80.5	2.6[b] ± 0.8		4.6[b] ± 0.8		4.5[b] ± 0.7	
2,3-Dimethylpentane	89.8	1.4 ± 0.5		2.6 ± 0.8	2.9 ±0.5	3.2 ± 0.8	3.6 ±0.5
2-Methylhexane	90.1			0.3 ± 0.1		0.4 ± 0.2	
3-Methylhexane	92.0						
2,2,4-Trimethylpentane	99.2	35.6 ± 1.0		30.5 ± 0.5		31.4 ± 0.7	
2,5-Dimethylhexane	109.1	7.2[c] ± 1.8	9.0 ± 1.5	8.4[c] ± 1.5	10.9 ± 1.0	8.3[c] ± 1.5	9.4 ± 1.0
2,4-Dimethylhexane	109.4			2.5 ± 1.0		1.1 ± 0.6	
2,2,3-Trimethylpentane	109.8	1.8 ± 1.2					
2,3,4-Trimethylpentane	113.5	15.7 ± 2.0	35.4 ±2.0	10.4 ± 2.0	24.6 ±2.0	14.9 ± 2.0	30.0 ± 1.5
2,3,3-Trimethylpentane	114.8	16.9 ± 2.0		11.9 ± 2.0		12.5 ± 2.0	
2,3-Dimethylhexane	115.6	2.8[d] ± 1.4		2.3[d] ± 1.1		1.9 ± 0.9	
3,4-Dimethylhexane	117.7					0.7 ± 0.4	
2,2,5-Trimethylhexane	124.1	2.4 ± 0.8		4.4 ± 1.5		3.4 ± 1.0	
Isononanes	127–143	0.6 ± 0.4		1.6 ± 0.8		1.1 ± 0.6	
Isoparaffins	143–151			0.6 ± 0.4			
Isoparaffins	143–160	1.1 ± 0.6					
Isoparaffins	147–152					2.3 ± 1.0	
Isoparaffins	151–160			0.4 ± 0.4			
Isoparaffins	>152					5.4 ± 0.5	
Isoparaffins	160–175	1.8 ± 0.8		1.5 ± 1.0			
Isoparaffins	>175	4.9 ± 0.8		11.8 ± 2.5			
Total		100.0		100.0		100.0	

[a] May include a small amount of 2,2-dimethylbutane.
[b] May include a small amount of 2,2,3-trimethylbutane.
[c] May include a small amount of 2,2-dimethylhexane.
[d] May include a small amount of 3,4-dimethylhexane.

Table 7 - Analyses of eight hydrocodimers

Components	Boiling point at 1 atm.	Hydrocodimer (hot acid) Sample 35 (see figure 22)	Hydrocodimer (cold phosphoric-acid) Sample 4 (see figure 3)	Hydrocodimer (phosphoric-acid) Sample 33 (see figure 20)	Hydrocodimer (Lawrenceville) Sample 36 (see figure 23)	Hydrocodimer (Tulsa) Sample 37 (see figure 24)	Hydrocodimer (Lima 6) Sample 41 (see figure 25)	Hydrocodimer (Lima 7) Sample 42 (see figure 26)	Hydrocodimer (MSO-1684) Sample 44 (see figure 28)
	°C	Percentage by volume (above pentanes)							
Cyclopentane	49.3								
2,2-Dimethylbutane	49.7								
2,3-Dimethylbutane	58.0								
2-Methylpentane	60.3	0.2 ± 0.1	0.7 ± 0.5	0.10 ± 0.05 0.10 ± 0.05	0.8 ± 0.4	0.2[a] ± 0.1	0.5 ± 0.3	0.5 ± 0.3	0.8 ± 0.3
3-Methylpentane	63.3			1.4 ± 0.7		2.6 ± 0.8			
n-Hexane	68.7					0.2[a] ± 0.1			
Methylcyclopentane	71.8					0.03[b] ± 0.03			
Benzene	80.1								
Heptanes	79-92	1.0 ± 0.5							
		1.2 ±0.5		1.6 ±0.7		3.0 ±0.8			
2,2-Dimethylpentane	79.2								
2,4-Dimethylpentane	80.5		1.2[b] ± 0.5		1.0[b] ± 0.6	3.6[b] ± 0.8	0.6[b] ± 0.3	0.7[b] ± 0.4	2.6[b] ± 0.5
2,3-Dimethylpentane	89.8			0.9[b] ± 0.5					
3-Methylhexane	90.1		1.1 ± 0.4		1.7[c] ± 0.8	15.0 ± 1.5	1.4[c] ± 0.7	1.3[c] ± 0.7	7.4[c] ± 0.6
2-Methylhexane	92.0		0.4 ± 0.3			1.2 ± 0.8		0.5 ± 0.1	
			1.5 ±0.5			16.2 ±0.8		1.5 ±0.7	
Olefins	>90								0.1 ± 0.0[5]
Olefins	90-99								0.1 ± 0.0[5]
Olefins	36-99		0.2 ± 0.1						
2,2,4-Trimethylpentane	99.2	35.4 ± 1.0	9.9 ± 0.8	12.1 ± 1.0	6.6 ± 1.0	7.2 ± 1.5	11.2 ± 1.5	5.2 ± 1.0	27.4 ± 1.0
Olefins	99-110	0.6 ± 0.3	1.5 ± 0.3						0.6 ± 0.3
Toluene	110.6					0.05[b] ± 0.03			
2,2-Dimethylhexane	106.8	4.0 ± 1.5	1.2 ± 0.6	2.7 ± 1.4	2.3 ± 1.0	1.8 ± 1.0	2.1 ± 1.0	1.8 ± 0.9	0.9 ± 0.5
2,5-Dimethylhexane	109.1	0.9 ± 0.7	6.7 ± 2.0	2.9 ± 1.7	4.8 ± 2.0	2.4 ± 1.2	1.8 ± 1.2	7.4 ± 1.5	2.2 ± 1.1
2,4-Dimethylhexane	109.4	26.0 ± 2.0	9.2 ± 3.0	11.8 ± 2.7	10.6 ± 2.5	8.5 ± 1.5	14.8 ± 2.0	10.0 ± 2.0	7.9 ± 1.5
2,2,3-Trimethylpentane	109.8	26.9±2.0	17.1 ±2.0	17.4 ± 1.5	15.4 ± 2.0	12.8 ± 1.5	18.7 ± 1.5	11.2 ± 1.5	11.0 ± 1.5
Olefins	>49					0.05 ± 0.03			
Olefins	49-110				0.1 ± 0.0[5]				
Olefins	110-114	0.8 ± 0.4					0.08 ± 0.04	0.2 ± 0.1	
Olefins	110-113.4		0.3 ± 0.1						0.2 ± 0.1
Olefins	113.4-114.7		0.4 ± 0.1						
Olefins	110-140				0.1 ± 0.0[5]				
Olefins	>110						0.09 ± 0.05	0.2 ± 0.1	
2,3,4-Trimethylpentane	113.5	19.0 ± 2.0	43.9 ± 2.0	43.4 ± 4.3	43.9 ± 2.0	34.9 ± 2.5	39.2 ± 3.0	37.3 ± 2.5	28.3 ± 2.0
2,3,3-Trimethylpentane	114.8	7.0 ± 1.5	8.6 ± 2.0	15.0 ± 3.0	6.1 ± 2.0	5.2 ± 1.5	7.2 ± 2.0	4.6 ± 1.5	3.1 ± 1.0
2,3-Dimethylhexane	115.6	1.4[d] ± 0.7	5.6[d] ± 3.0	4.3[d] ± 2.1	6.5 ± 2.0	4.8 ± 1.5	4.3 ± 1.5	7.4 ± 2.0	1.9 ± 1.0
Olefins	114-120	27.4± 2.0	58.1 ±4.0	62.7 ± 2.0	56.5 ± 2.0	44.9 ± 2.0	50.7 ±2.0	49.3 ±2.0	0.6 ± 0.3
									33.3 ± 1.5
Olefins	114-115.6	0.6 ± 0.3							
Isoparaffins	>115.6	2.9 ± 0.8		5.3 ± 1.0					
Olefins	>115.6	0.2 ± 0.1							
		3.1 ±0.8							
Olefins	114.7-115.5		0.4 ± 0.1						
Olefins	115.5-117		0.6 ± 0.2						
3,4-Dimethylhexane	117.7				2.9[e] ± 0.9	5.3[e] ± 1.5	4.6[e] ± 1.5	3.9[e] ± 1.5	1.1[e] ± 0.6
Isoparaffins	117-120		1.9 ± 1.0						
Olefins	117-120		0.4 ± 0.1						
Olefins	>120								
Isononanes	120-132		2.0 ± 1.0						0.9 ± 0.4
Isononanes	122-127							1.7 ± 0.8	
Isononanes	127-135				2.9 ± 0.9	2.4 ± 1.2	2.4 ± 1.2	2.6 ± 1.2	
Isononanes	122-135								2.6 ± 0.8
Isononanes	122-144		0.2 ± 0.1						
Olefins	>132		3.6 ± 0.6						
Isoparaffins	>132				2.6 ± 0.8	0.05[b] 0.03	0.07 ± 0.03	0.08 ± 0.04	
Isononanes	135-140					4.5 ± 0.8	3.1[3] ± 1.0	3.8 ± 1.2	
Aromatics	136-145					4.55±0.8	3.2 ± 1.0	0.07 ± 0.04	3.9 ± 1.2
Isoparaffins	>135							11.0 ± 1.0	
Aromatics	>140				7.1 ± 0.8		6.5 ± 0.8		11.1 ± 1.0
Isoparaffins	>140								
Isoparaffins	145-165								1.3 ± 0.6
Isoparaffins	165-177.8								2.9 ± 0.9
Isoparaffins	>177.8								7.5 ± 0.6
Total		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

[a] Hydrocodimer apparently contaminated as with naphtha
[b] May include a small amount of 2,2,3-trimethylbutane
[c] May include a small amount of methylhexanes
[d] May include a small amount of 3,4-dimethylhexane
[e] May include some other olefins

TABLE 8.—*Comparison of the analysis of the octanes in the butene alkylate, sample 24, by several laboratories*

[Values are percentage by volume (above pentanes)]

Components	API Research Project 6 (November 30, 1943)	Standard Oil Co. (Ind.) (July 29, 1943)	Shell Oil Co. (February 22, 1944)
2, 2, 4-Trimethylpentane	35.5 ±0.5	35.8	35.1
2, 5-Dimethylhexane 2, 4-Dimethylhexane 2, 2, 3-Trimethylpentane	5.4 ±1.0	6.9	4.8
2, 3, 4-Trimethylpentane	24.0 ±2.0	24.1	25.5
2, 3, 3-Trimethylpentane	25.2 ±2.0	25.2	25.5
2, 3-Dimethylhexane	2.4 ±1.5	1.1	----

Table 9—Relative amounts of hexanes, heptanes, octanes, and nonanes and higher paraffins, in 20 alkylates and 8 hydrocodimers.

Sample No.	Material	Hexanes	Heptanes	Octanes	Nonanes plus Higher Paraffins	Total
		Relative amount by volume				
20	C_3 Alkylate (H_2SO_4)	5.3	65.7	18.0	11.0	100.0
17	C_3 Alkylate (HF)	5.0	41.5	29.7	23.8	100.0
16	C_3–C_4 Alkylate (HF)	2.3	10.2	60.3	27.2	100.0
1	C_4 Alkylate (H_2SO_4)	8.8	6.7	67.5	17.0	100.0
2	C_4 Alkylate (H_2SO_4)	12.6	1.3	63.7	12.4	100.0
9	C_4 Alkylate (H_2SO_4)	8.3	7.5	68.2	16.0	100.0
10	C_4 Alkylate (H_2SO_4)	9.4	7.7	73.1	9.8	100.0
24	C_4 Alkylate (H_2SO_4)	2.1	2.1	92.5	3.3	100.0
27	C_4 Alkylate (H_2SO_4)	6.8	7.0	67.0	19.2	100.0
13	C_4 Alkylate (HF)	2.1	4.5	83.6	9.8	100.0
15	C_4–C_5 Alkylate (HF)	1.5	3.5	65.2	29.8	100.0
11	C_4–C_5 Alkylate (H_2SO_4)	5.0	4.2	49.9	40.9	100.0
7	C_5 Alkylate (H_2SO_4)	5.8	3.5	30.6	60.1	100.0
12	C_5 Alkylate (H_2SO_4)	6.0	3.8	28.7	61.5	100.0
22	C_5 Alkylate (H_2SO_4)	3.2	2.4	45.9	48.5	100.0
23	C_5 Alkylate (H_2SO_4)	4.4	3.2	36.5	55.9	100.0
14	C_5 Alkylate (HF)	1.6	3.3	39.6	55.5	100.0
34	Dimer (hot acid) Alkylate (H_2SO_4)	4.9	4.3	80.0	10.8	100.0
21	Trimer (hot acid) Alkylate (H_2SO_4)	5.9	7.8	66.0	20.3	100.0
43	Trimer (cold acid) Alkylate (H_2SO_4)	8.4	8.6	70.8	12.2	100.0
35	Hydrocodimer (hot acid)	0.2	1.0	95.8	3.0	100.0
4	Hydrocodimer (solid phosphoric acid)	0.7	2.8	90.7	5.8	100.0
33	Hydrocodimer (phosphoric acid)	1.5	0.9	92.3	5.3	100.0
36	Hydrocodimer (Lawrenceville)	0.8	2.7	83.9	12.6	100.0
37	Hydrocodimer (Tulsa)	2.6	19.9	70.6	6.9	100.0
41	Hydrocodimer (Lima 6)	0.5	2.0	85.5	12.0	100.0
42	Hydrocodimer (Lima 7)	0.5	3.2	78.1	19.2	100.0
44	Hydrocodimer (HSO 1684)	0.8	10.1	74.6	14.5	100.0

Table 10 — Relative amount of 2,3-dimethylbutane in the hexane fraction of 15 alkylates.

Sample No.	Material	2,3-Dimethylbutane	2,2-Dimethylbutane plus 2-Methylpentane plus 3-Methylpentane	Total
		Relative amount by volume		
20	C_3 Alkylate (H_2SO_4)	66.0	34.0	100
17	C_3 Alkylate (HF)	58.0	42.0	100
16	C_3–C_4 Alkylate (HF)	60.9	39.1	100
1	C_4 Alkylate (H_2SO_4)	62.5	37.5	100
2	C_4 Alkylate (H_2SO_4)	64.5	35.5	100
9	C_4 Alkylate (H_2SO_4)	78.3	21.7	100
10	C_4 Alkylate (H_2SO_4)	74.5	25.5	100
27	C_4 Alkylate (H_2SO_4)	76.5	23.5	100
11	C_4 –C_5 Alkylate (H_2SO_4)	56.0	44.0	100
7	C_5 Alkylate (H_2SO_4)	44.8	55.2	100
12	C_5 Alkylate (H_2SO_4)	45.0	55.0	100
23	C_5 Alkylate (H_2SO_4)	47.7	52.3	100
34	Dimer (hot acid) Alkylate (H_2SO_4)	69.4	30.6	100
21	Trimer (hot acid) Alkylate (H_2SO_4)	71.2	28.8	100
43	Trimer (cold acid) Alkylate (H_2SO_4)	78.6	21.4	100
	Average	64±10	36±10	100

Table II—Relative amounts of the heptanes in 20 alkylates and 7 hydrocodimers

Sample No.	Material	2,2-Dimethyl-pentane	2,4-Dimethyl-pentane	2,3-Dimethyl-pentane	2-Methylhexane plus 3-Methylhexane	Total
		Relative amount by volume				
20	C_3 Alkylate (H_2SO_4)	1.7	39.9	54.9	3.5	100.0
17	C_3 Alkylate (HF)	1.9	44.0	51.0	3.1	100.0
16	C_3–C_4 Alkylate (HF)	6.9	41.2	44.1	7.8	100.0
1	C_4 Alkylate (H_2SO_4)	—	53.7	32.9	13.4	100.0
2	C_4 Alkylate (H_2SO_4)	6.2	48.7	30.1	15.0	100.0
9	C_4 Alkylate (H_2SO_4)	6.7	56.0	28.0	9.3	100.0
10	C_4 Alkylate (H_2SO_4)	10.4	50.6	32.5	6.5	100.0
24	C_4 Alkylate (H_2SO_4)	52.4		47.6		100.0
27	C_4 Alkylate (H_2SO_4)	2.9	52.9	37.1	4.3	97.2[a]
13	C_4 Alkylate (HF)	57.8		42.2		100.0
15	C_4–C_5 Alkylate (HF)	51.4		48.6		100.0
11	C_4–C_5 (H_2SO_4)	54.8		26.2	19.0	100.0
7	C_5 Alkylate (H_2SO_4)	51.4		48.6		100.0
12	C_5 Alkylate (H_2SO_4)	55.3		44.7		100.0
22	C_5 Alkylate (H_2SO_4)	62.5		37.5		100.0
23	C_5 Alkylate (H_2SO_4)	53.1		31.3	15.6	100.0
14	C_5 Alkylate (HF)	42.4		57.6		100.0
34	Dimer (hot acid) Alkylate (H_2SO_4)	7.0	60.5	32.5		100.0
21	Trimer (hot acid) Alkylate (H_2SO_4)	3.8	59.0	33.3	3.9	100.0
43	Trimer (cold acid) Alkylate (H_2SO_4)	5.8	52.3	37.2	4.7	100.0
4	Hydrocodimer (solid phosphoric acid)	44.4		40.8	14.8	100.0
33	Hydrocodimer (phosphoric acid)	6.7		93.3		100.0
36	Hydrocodimer (Lawrenceville)	37.0		63.0		100.0
37	Hydrocodimer (Tusla)	18.2		75.7	6.1	100.0
41	Hydrocodimer (Lima 6)	30.0		70.0		100.0
42	Hydrocodimer (Lima 7)	31.8		61.4	6.8	100.0
44	Hydrocodimer (HSO 1684)	24.5		75.5		100.0

[a] Contained also some 2,2,3-trimethylbutane, relative amount 2.8.

Table 12 — Relative amounts of the octanes in 20 alkylates and 8 hydrocodimers.

Sample No.	Material	2,2,4-Trimethylpentane	2,2-Dimethylhexane	2,5-Dimethylhexane plus 2,4-Dimethylhexane	2,2,3-Trimethylpentane	2,3,4-Trimethylpentane	2,3,3-Trimethylpentane	2,3-Dimethylhexane	3,4-Dimethylhexane	Total
		Relative amount by volume								
20	C_3 Alkylate (H_2SO_4)	43.5		13.9	4.4	13.9	17.8	6.7		100.0
17	C_3 Alkylate (HF)	55.1		13.5	3.7	11.5	13.2	3.0		100.0
16	C_3 – C_4 Alkylate (HF)	49.9		15.1	3.8	11.3	11.1	6.6	2.2[a]	100.0
1	C_4 Alkylate (H_2SO_4)	44.5		12.0	2.7	13.8	21.5	5.5		100.0
2	C_4 Alkylate (H_2SO_4)	35.2		16.2	3.0	24.0	16.3	5.3		100.0
9	C_4 Alkylate (H_2SO_4)	38.0		11.8	2.5	24.0	17.7	6.2		100.0
10	C_4 Alkylate (H_2SO_4)	36.7		11.3	2.2	26.3	20.4	3.1		100.0
24	C_4 Alkylate (H_2SO_4)	38.4		3.7	2.2	25.9	27.2	2.6		100.0
27	C_4 Alkylate (H_2SO_4)	39.9	0.4	10.8	1.9	21.3	20.2	4.9	0.6	100.0
13	C_4 Alkylate (HF)	49.9		16.0	3.5	11.2	12.0	7.4		100.0
15	C_4 – C_5 Alkylate (HF)	51.1		15.5	3.2	10.9	12.4	6.9		100.0
11	C_4 – C_5 Alkylate (H_2SO_4)	40.5		10.7	1.6	23.3	20.5	3.4		100.0
7	C_5 Alkylate (H_2SO_4)	43.0		14.1	2.9	21.6	14.8	3.6		100.0
12	C_5 Alkylate (H_2SO_4)	43.4		14.3	2.4	14.7	24.5	0.7		100.0
22	C_5 Alkylate (H_2SO_4)	47.3		8.1	1.5	20.5	20.7	1.9		100.0
23	C_5 Alkylate (H_2SO_4)	47.4		10.7	2.2	17.6	19.6	2.5		100.0
14	C_5 Alkylate (HF)	61.1		9.9	1.8	13.6	10.6	3.0		100.0
34	Dimer (hot acid) Alkylate (H_2SO_4)	44.5		9.0	2.3	19.6	21.1	3.5		100.0
21	Trimer (hot acid) Alkylate (H_2SO_4)	46.2		12.7	3.8	15.8	18.0	3.5		100.0
43	Trimer (cold acid) Alkylate (H_2SO_4)	44.4		11.7	1.9	21.0	17.7	2.7	1.0[a]	100.0
33	Hydrocodimer (hot acid)	37.7	4.3	1.0	27.7	20.3	7.5	1.5	[b]	100.0
4	Hydrocodimer (cold phosphoric acid)	11.4	1.4	7.7	10.6	50.4	9.9	6.4	2.2[a]	100.0
33	Hydrocodimer (phosphoric acid)	13.1	2.9	3.1	12.8	47.1	16.3	4.7	[b]	100.0
36	Hydrocodimer (Lawrenceville)	7.9	2.8	5.7	12.7	52.4	7.3	7.7	3.5[a]	100.0
37	Hydrocodimer (Tulsa)	10.3	2.6	3.5	12.1	49.7	7.4	6.8	7.6[a]	100.0
41	Hydrocodimer (Lima 6)	13.1	2.5	2.1	17.4	46.0	8.5	5.0	5.4[a]	100.0
42	Hydrocodimer (Lima 7)	6.7	2.3	9.6	12.9	48.1	5.9	9.5	5.0[a]	100.0
44	Hydrocodimer (HSO 1684)	37.6	1.2	3.0	10.9	38.9	4.3	2.6	1.5[a]	100.0

[a] May include some other octanes. [b] Some 3,4-dimethylhexane not included.

Table 13 — Relative amounts of two nonanes (trimethylhexanes) in 11 alkylates

Sample No.	Material	2,2,5-Trimethylhexane	2,3,5-Trimethylhexane	Total
		Relative amount by volume		
16	C_3 – C_4 Alkylate (HF)	81.8	18.2	100
1	C_4 Alkylate (H_2SO_4)	87.0	13.0	100
2	C_4 Alkylate (H_2SO_4)	82.2	17.8	100
27	C_4 Alkylate (H_2SO_4)	83.0	17.0	100
15	C_4 – C_5 Alkylate (HF)	83.2	16.8	100
11	C_4 – C_5 Alkylate (H_2SO_4)	80.5	19.5	100
7	C_5 Alkylate (H_2SO_4)	83.8	16.2	100
12	C_5 Alkylate (H_2SO_4)	80.1	19.9	100
22	C_5 Alkylate (H_2SO_4)	81.9	18.1	100
23	C_5 Alkylate (H_2SO_4)	84.0	16.0	100
14	C_5 Alkylate (HF)	84.2	15.8	100
	Average	82.9 ± 1.5	17.1 ± 1.5	100

Table 14—Summary of the results of the cooperative analyses of the butene alkylate, Sample 27.

Components	Boiling Point at 1 atm.	API RP6 (Oct. 15, 1944)		Std. Oil Dev. (Jan. 2, 1945) (Infrared)	Atlantic (June 22, 1945) (Mass)	Sec. - Vac. (July 25, 1945) (Infrared)	Sun Oil (Oct. 8, 1945) (Raman)	U. O. P. (April 24, 1946) (Infrared)	Phillips (June 20, 1946) (Infrared)
	°C	Percentage by volume of the total alkylate							
Isobutane	−11.7	8.3 ± 0.5	6.2 ± 0.5	8.2	8.02 [a]	8.00 [b]	7.6	8.20 [c]	8.00 [d]
n-Butane	−0.5				0.34	0.31		0.25	0.37
Neopentane	9.5				0.06	0.07			0.09
Isopentane	27.9								
n-Pentane	36.1	0.6 ± 0.3		0.4	0.35	0.40		0.43	0.46
2,2-Dimethylbutane	49.7	0.0		0.0	0.0	0.00		0.02	0.0
2,3-Dimethylbutane	58.0	4.7 ± 0.8		4.4	4.84	4.82		4.72	4.76
2-Methylpentane	60.3	1.1 ± 0.5		1.2	1.02	1.00		0.98	1.00
3-Methylpentane	63.3	0.4 ± 0.2		1.1	0.42	0.43		0.46	0.45
2,2-Dimethylpentane	79.2	0.2 ± 0.2		0.0	*	0.00		0.00	0.02
2,4-Dimethylpentane	80.5	3.4 ± 0.9	3.8 ± 0.5	3.4	3.55	3.49	3.4 [f]	3.56	3.50
2,2,3-Trimethylbutane	80.9	0.2 ± 0.2		0.2	*	0.20	0.27	0.28	0.25
2,3-Dimethylpentane	89.8	2.3 ± 0.6		2.4	2.32	2.71	2.6	2.44	2.25
2-Methylhexane	90.1	0.3 ± 0.2	2.6 ± 0.5	0.1	0.18	0.07	0.2	0.10	0.16
3-Methylhexane	92.0			0.2	0.15	0.04		0.06	0.13
2,2,4-Trimethylpentane	99.2	24.3 ± 0.9		24.6	24.4	24.28	24.1	24.40	24.41
2,2-Dimethylhexane	106.8	0.2 ± 0.2		0.0		0.05	7.6	0.10	0.08
2,5-Dimethylhexane	109.1	6.6 ± 1.4	8.0 ± 0.9	4.3	4.48	4.37		4.46	4.43
2,4-Dimethylhexane	109.4			3.0	2.70	2.70		2.76	2.83
2,2,3-Trimethylpentane	109.8	1.2 ± 0.6		1.3	1.21	1.02	1.1	1.34	1.21
2,3,4-Trimethylpentane	113.5	13.0 ± 1.8		12.0	12.4	12.73	12.5	12.38 [e]	12.62
2,3,3-Trimethylpentane	114.8	12.3 ± 1.8	28.7 ± 1.4	12.7	12.3 [f]	12.64	12.7	12.49	12.25
2,3-Dimethylhexane	115.6	3.0 ± 1.4		3.1	3.0 [f]	2.49	3.3	2.56	2.84
3,4-Dimethylhexane	117.7	0.4 ± 0.3		0.2		0.63		0.73	0.52
2,2,5-Trimethylhexane	124.1	4.5 ± 0.9				4.56	4.0 [f]	4.25	4.28
2,3,5-Trimethylhexane	131.4	0.9 ± 0.5							
Higher-boiling isoparaffins	>131.4	12.1 ± 0.5							
Total		100.0							

[a] 0.09 percent of pentenes also found.
[b] 0.08 percent of pentenes also found.
[c] 0.03 percent of olefins also found.
[d] Trace of 2-methyl-1-butene.
[e] The sum of 2,2-dimethylpentane and 2,2,3-trimethylbutane reported to be 0.25 percent.
[f] Corrected for a small amount of this component occurring in adjacent lots not analyzed by this laboratory.

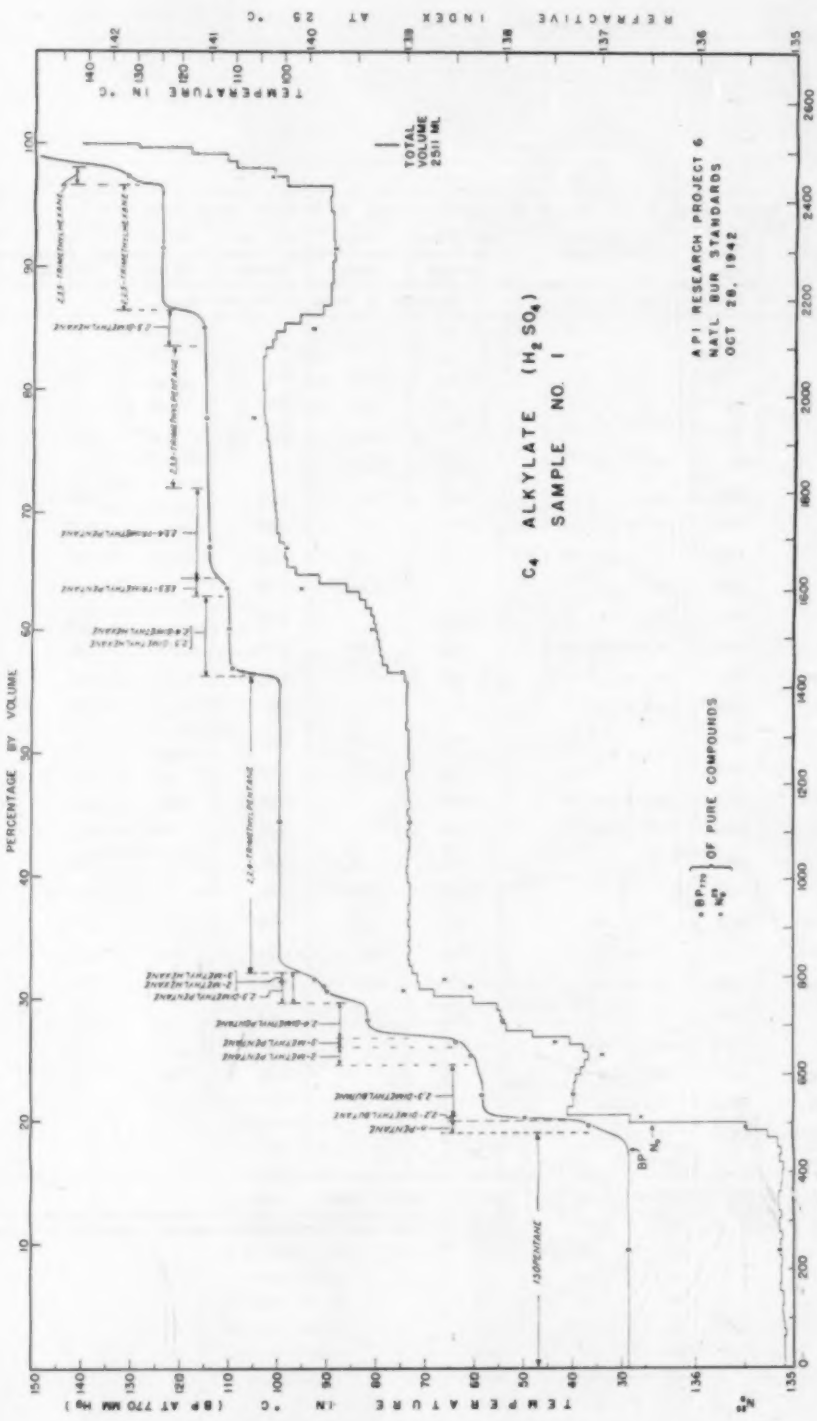

FIGURE 1.—*Results of the analytical distillation of C₄ alkylate (H_2SO_4), sample 1.*

Details are given in table 4.

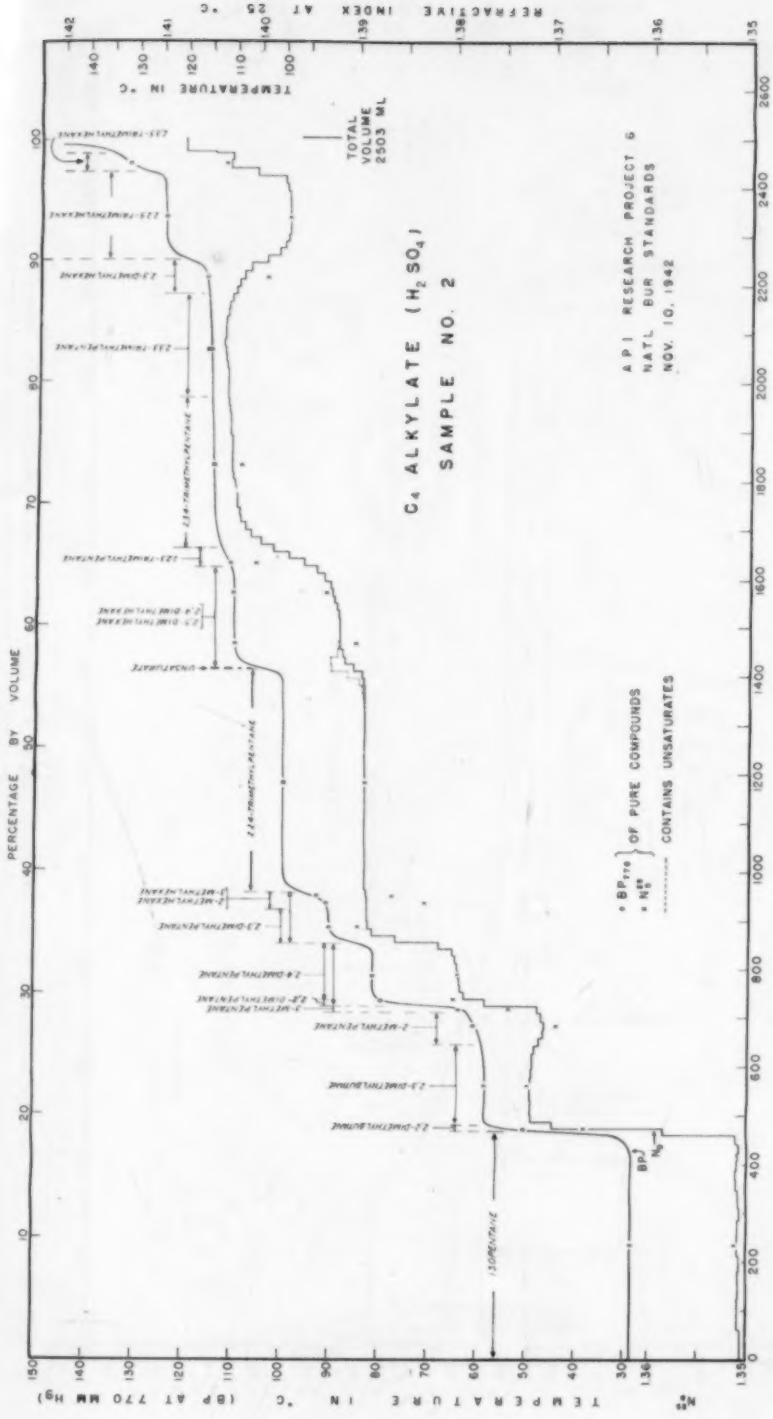

FIGURE 2.—*Results of the analytical distillation of* C_4 *alkylate* (H_2SO_4), *sample 2.*

Details are given in table 4.

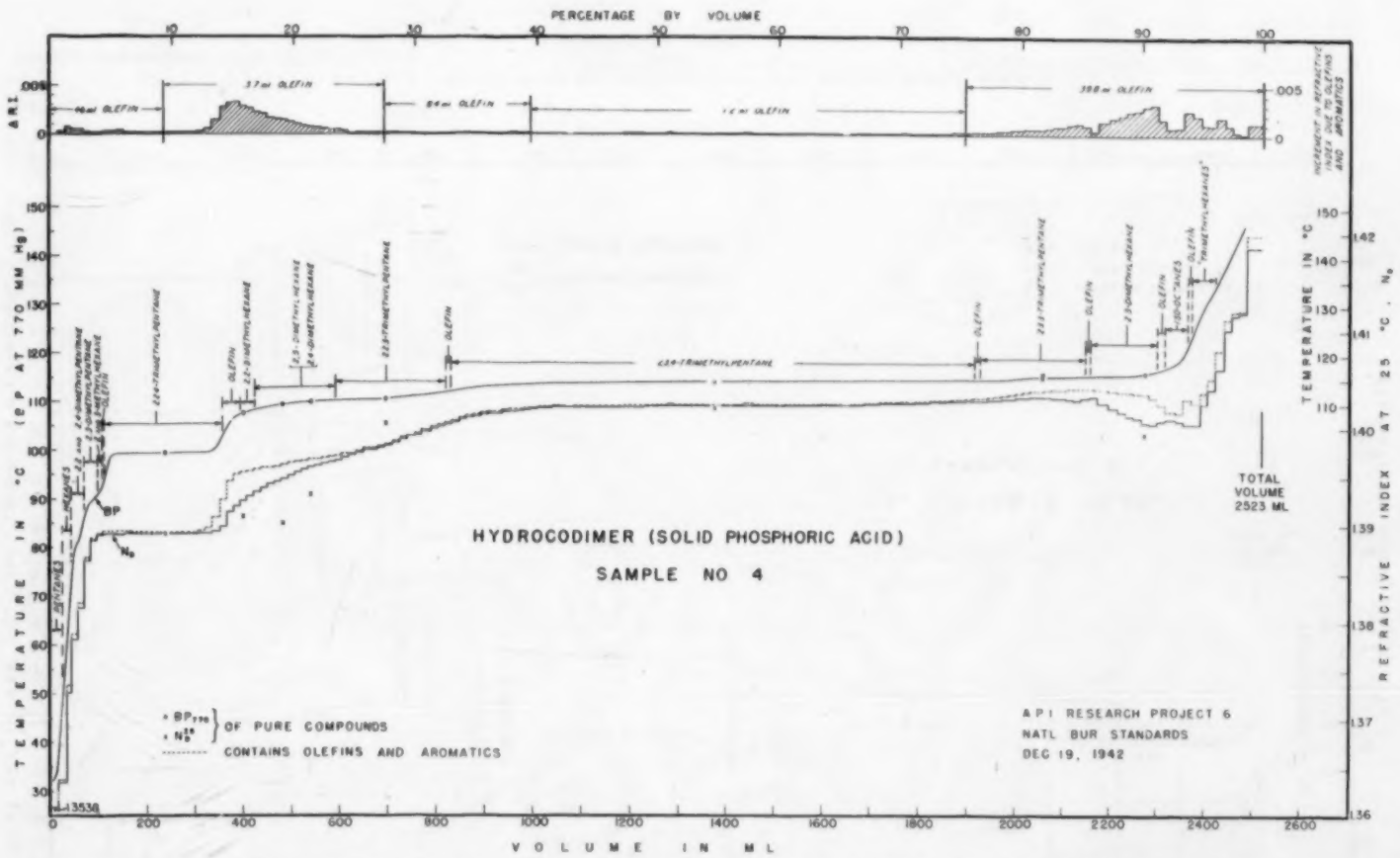

FIGURE 3.—*Results of the analytical distillation of hydrocodimer (solid phosphoric-acid), sample 4.*

The upper part of the figure gives the amounts of olefins from determinations of bromine numbers, and the shaded area gives the increment in refractive index caused by the presence of small amounts of olefins and smaller amounts of aromatics in this material. Details are given in table 7.

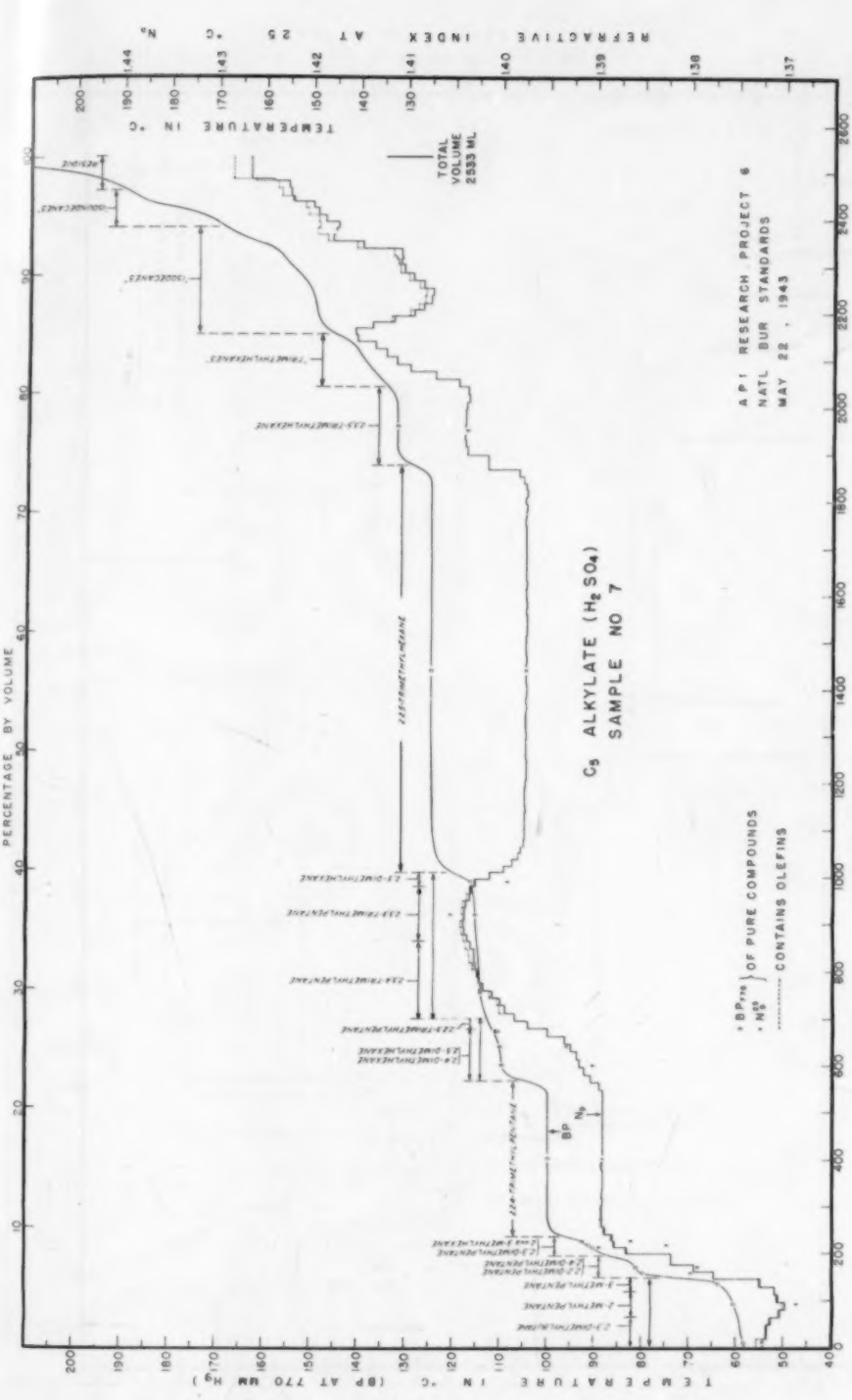

FIGURE 4.—*Results of the analytical distillation of* C_5 *alkylate* (H_2SO_4), *sample 7.*

Details are given in table 5.

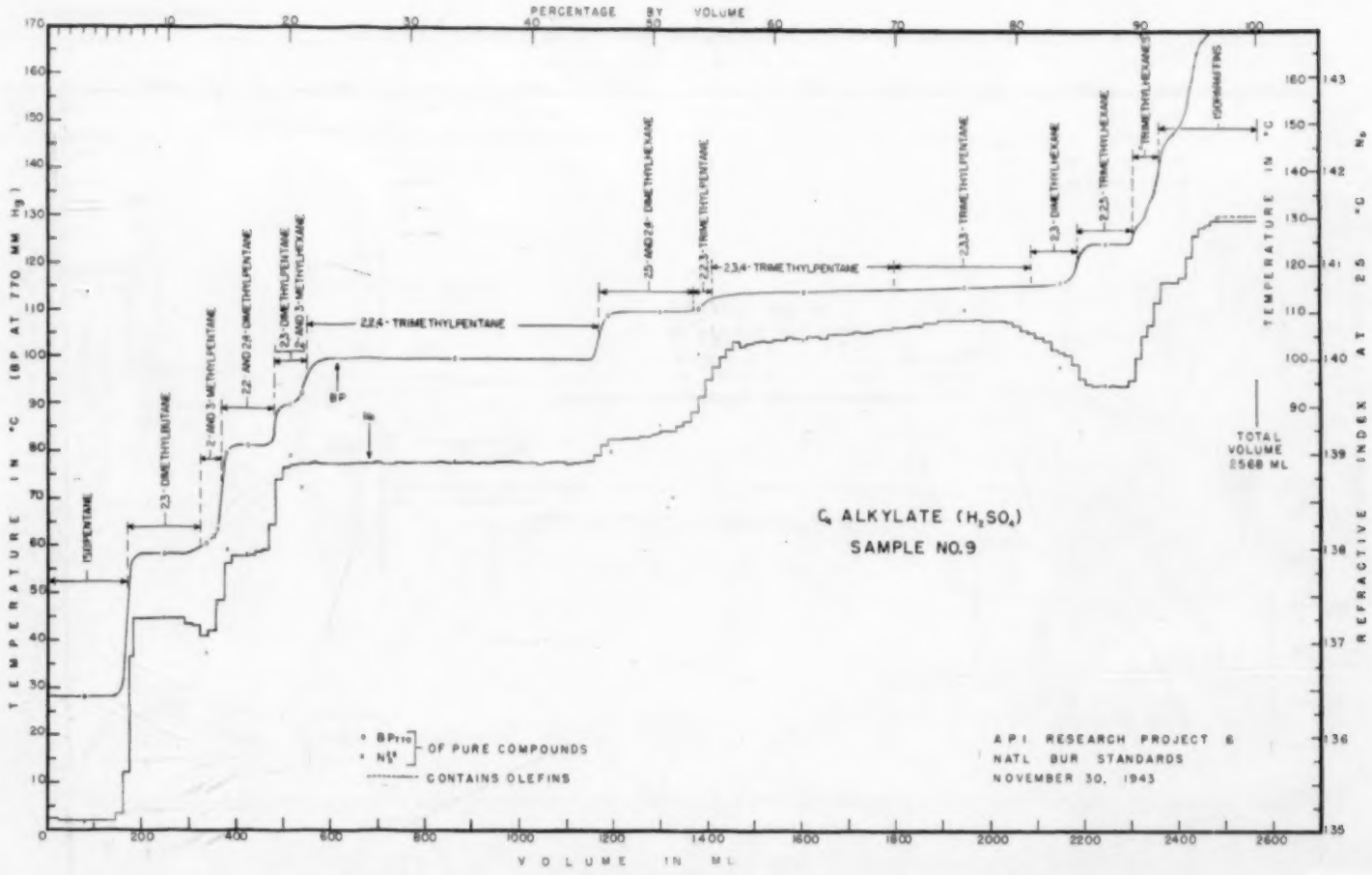

FIGURE 5.—*Results of the analytical distillation of* C_4 *alkylate* (H_2SO_4), *sample 9.*

Details are given in table 4.

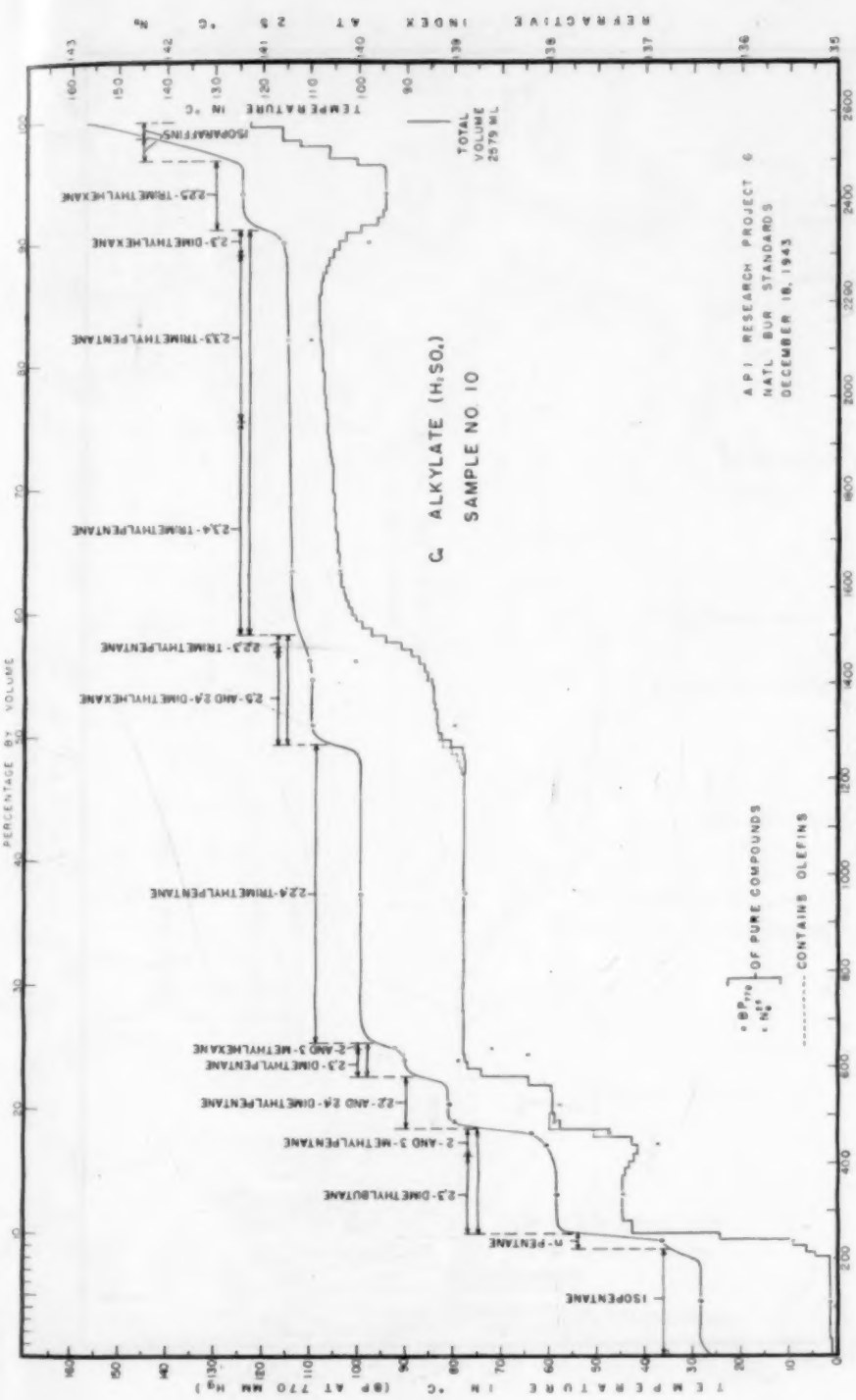

FIGURE 6.—*Results of the analytical distillation of C_4 alkylate (H_2SO_4), sample 10.*

Details are given in table 4.

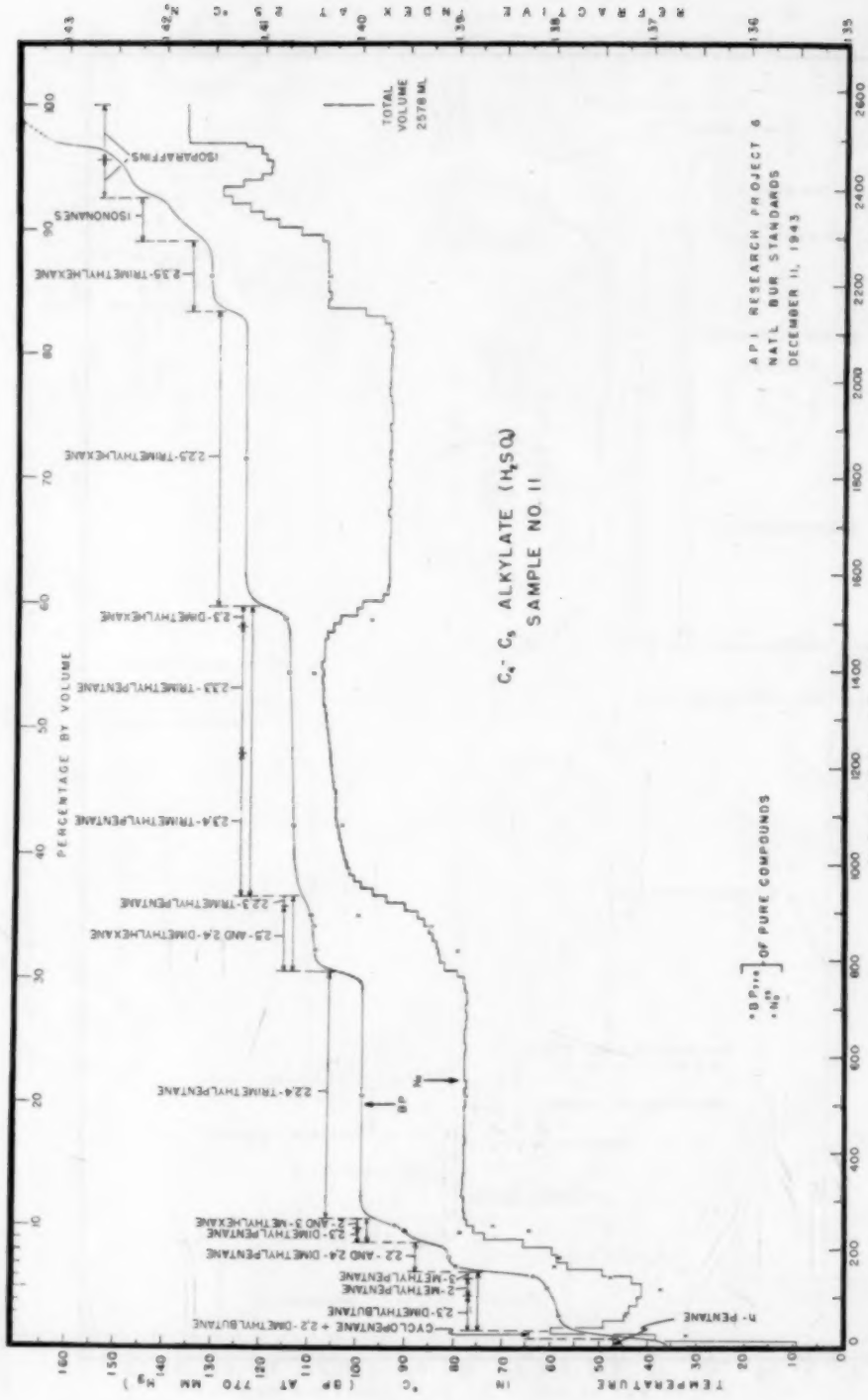

FIGURE 7.—*Results of the analytical distillation of C_4-C_5 alkylate (H_2SO_4), sample 11.*

Details are given in table 5.

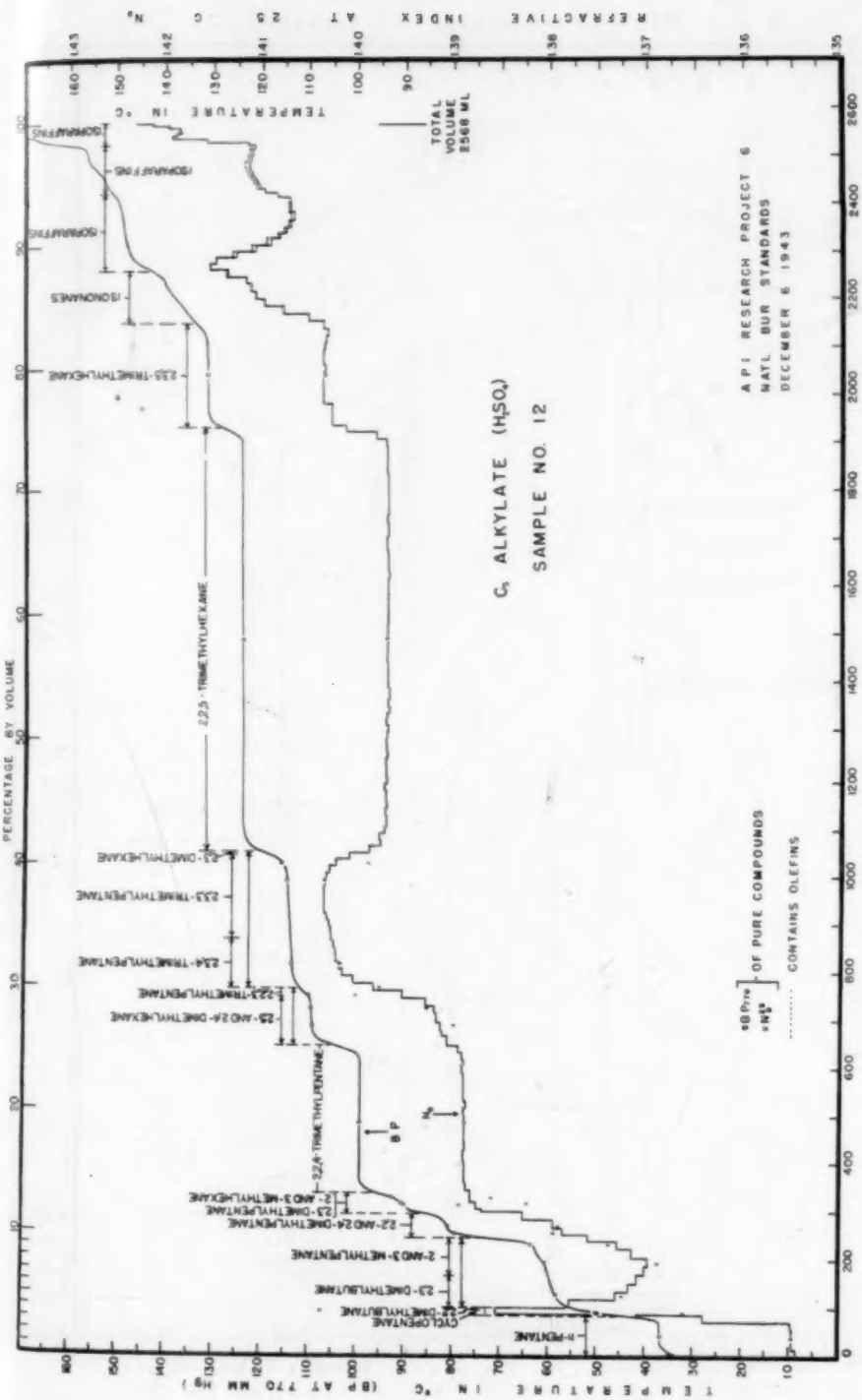

FIGURE 8.—*Results of the analytical distillation of* C_5 *alkylate* (H_2SO_4), *sample 12.*

Details are given in table 5.

FIGURE 7.—*Results of the analytical distillation of* C_4-C_5 *alkylate* (H_2SO_4), *sample 11.*

Details are given in table 5.

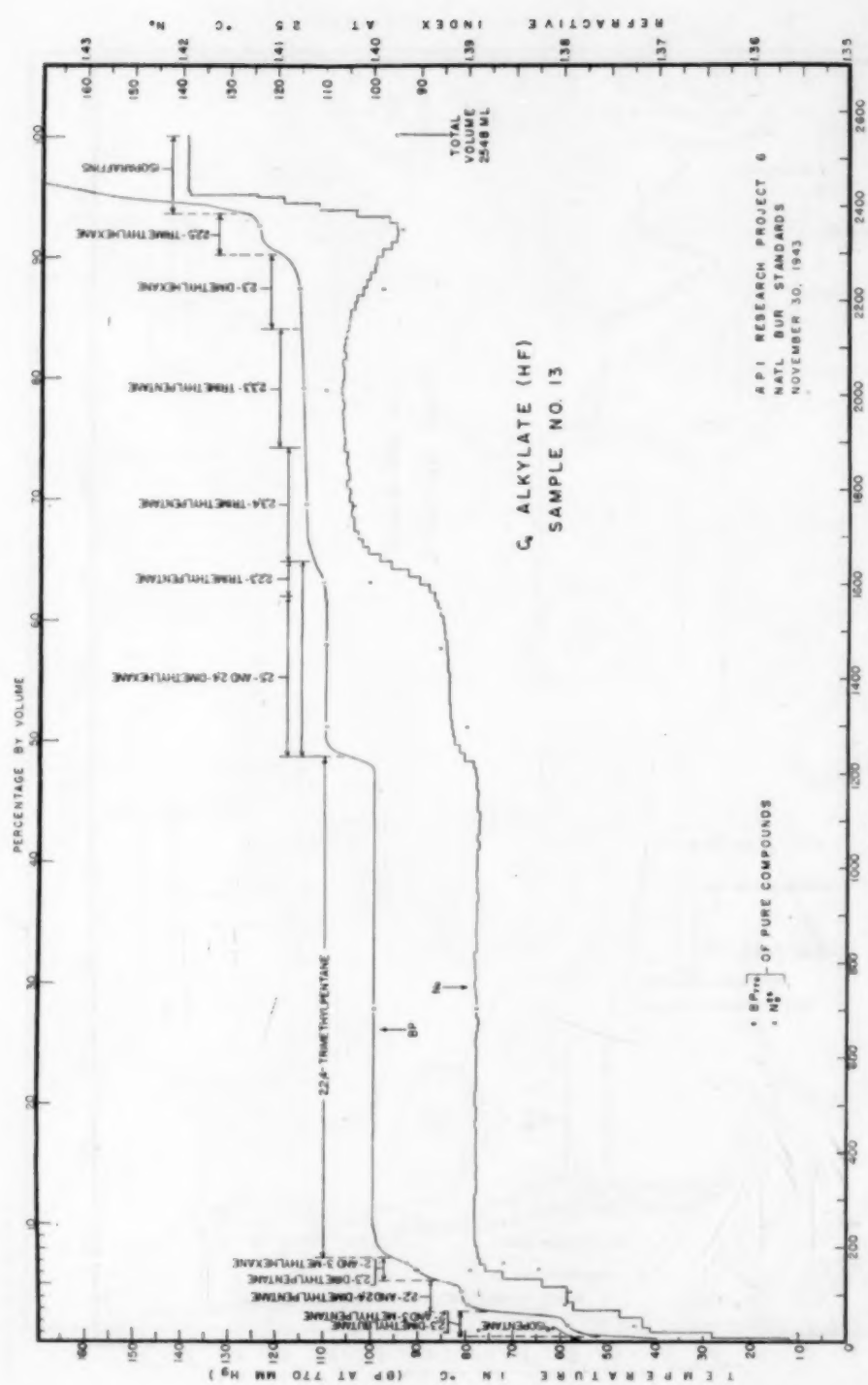

FIGURE 9.—*Results of the analytical distillation of* C_4 *alkylate* (HF), *sample 13.*

Details are given in table 4.

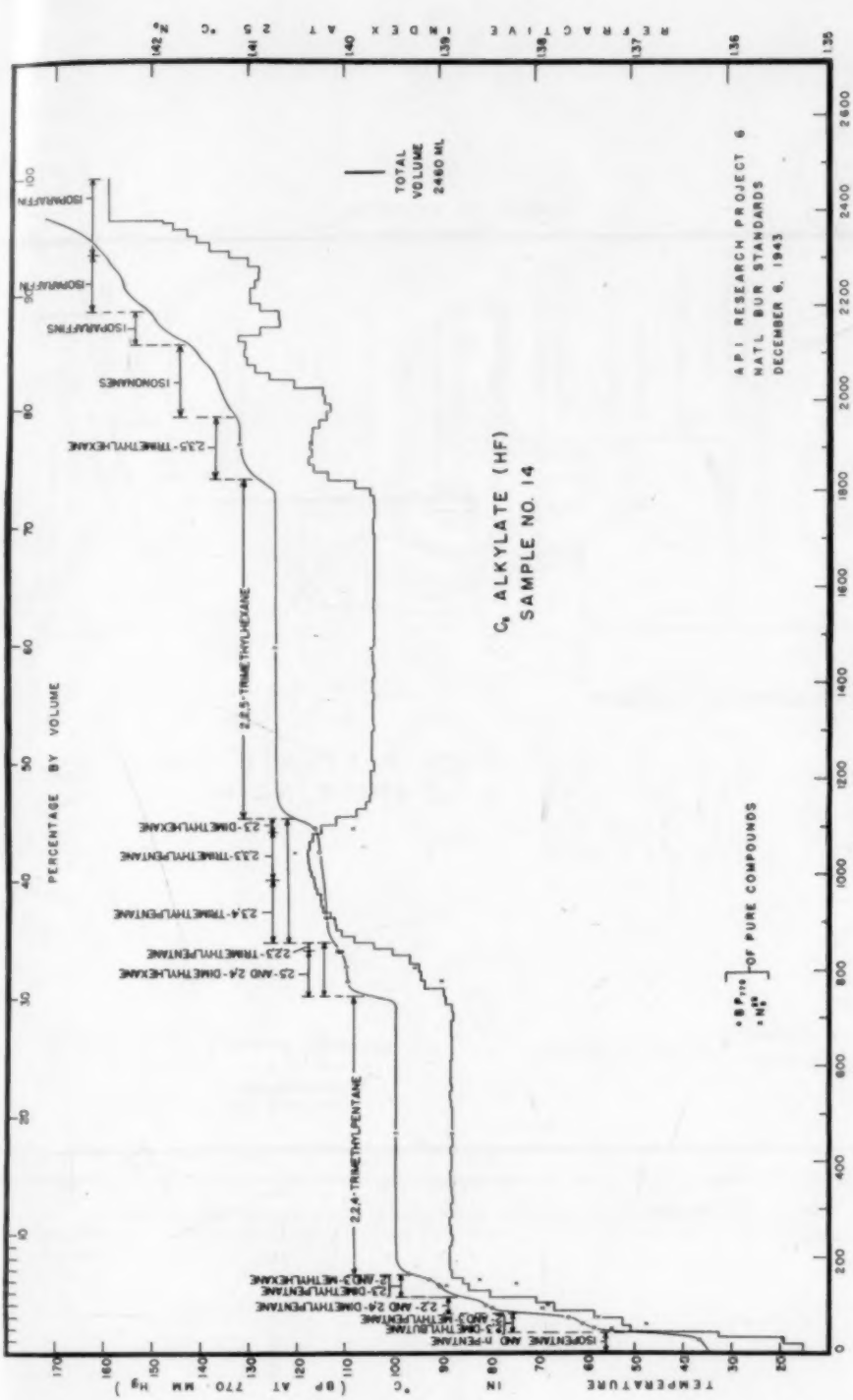

FIGURE 10.—*Results of the analytical distillation of* C_5 *alkylate* (HF), *sample 14.*

Details are given in table 5.

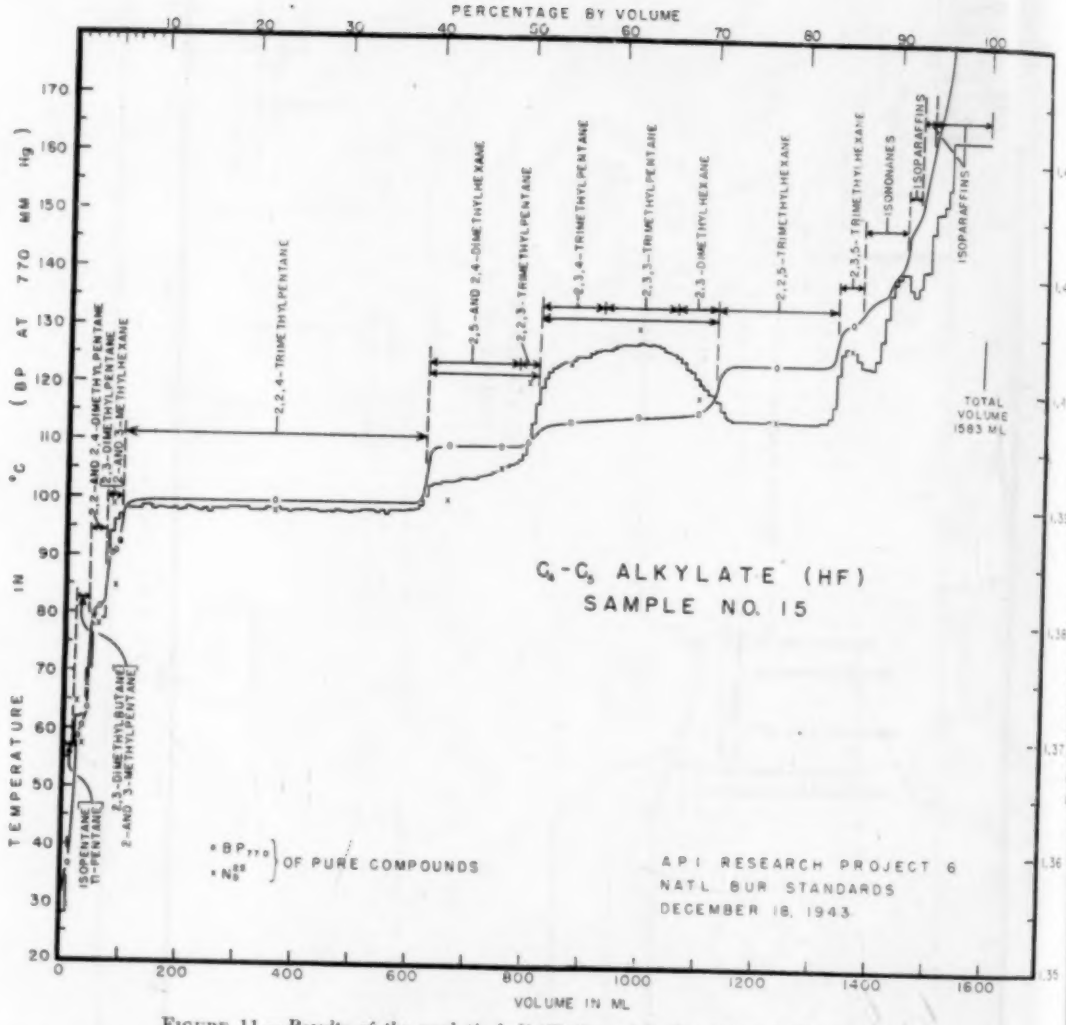

FIGURE 11.—*Results of the analytical distillation of* C_6-C_8 *alkylate* (HF), *sample 15.*

Details are given in table 5.

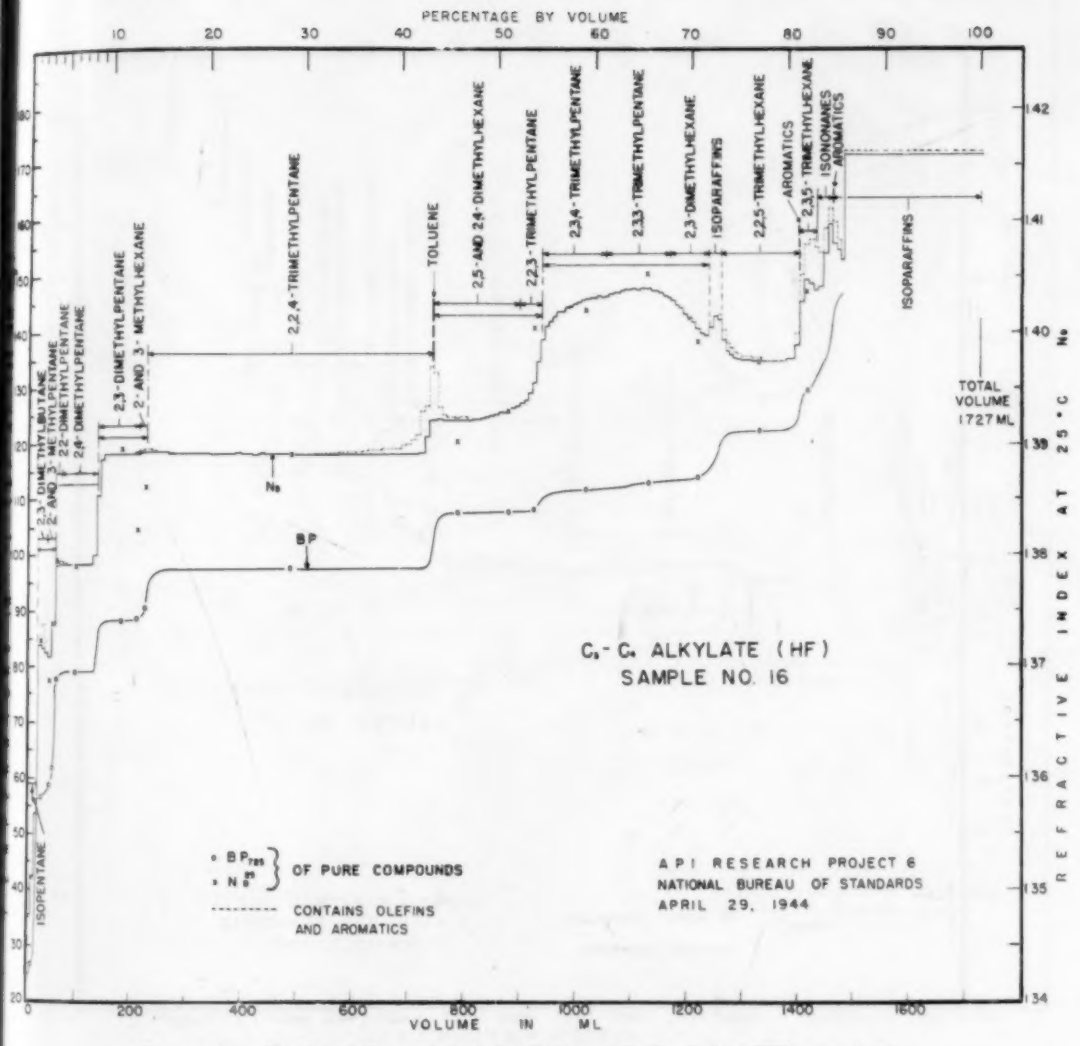

FIGURE 12.—*Results of the analytical distillation of* C_3-C_4 *alkylate* (HF), *sample 16.*

Details are given in table 3.

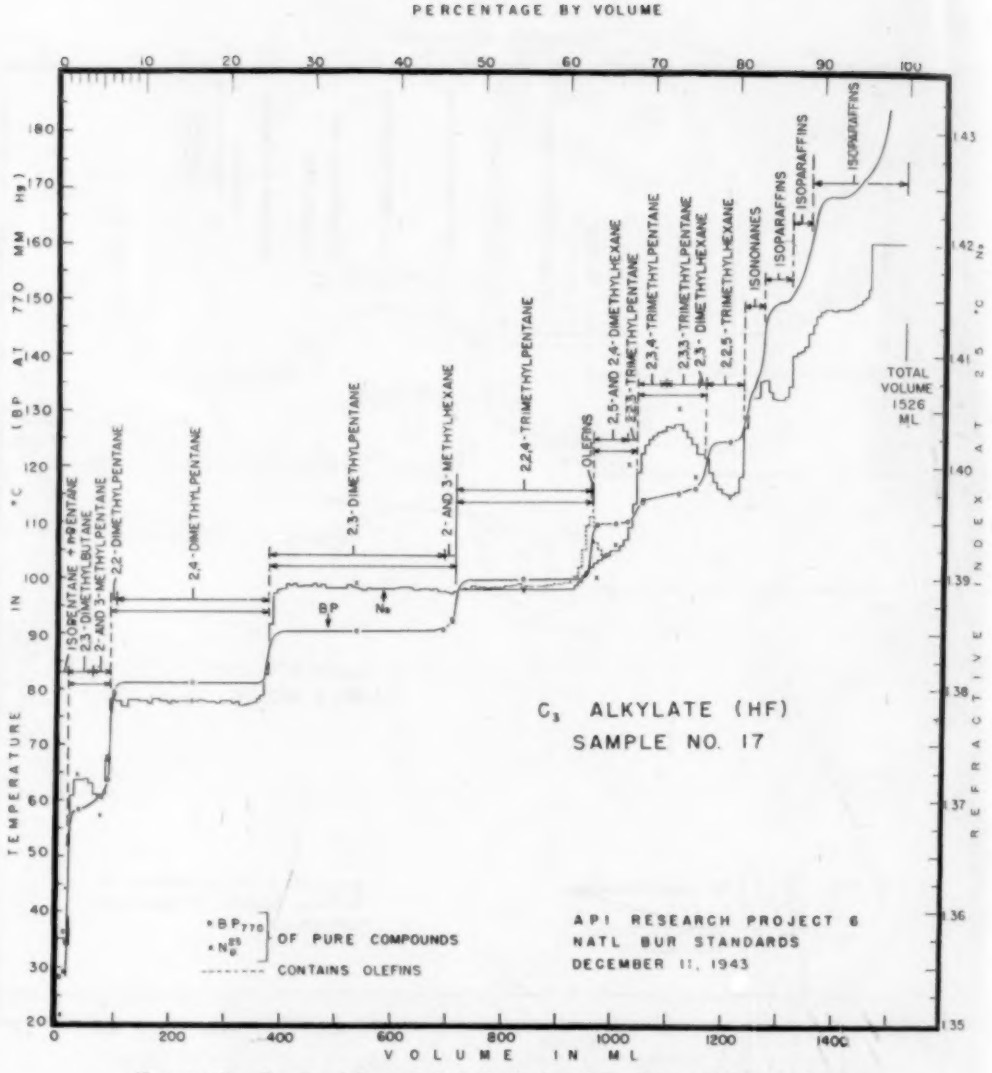

FIGURE 13.—*Results of the analytical distillation of* C_5 *alkylate* (HF), *sample 17.*

Details are given in table 3.

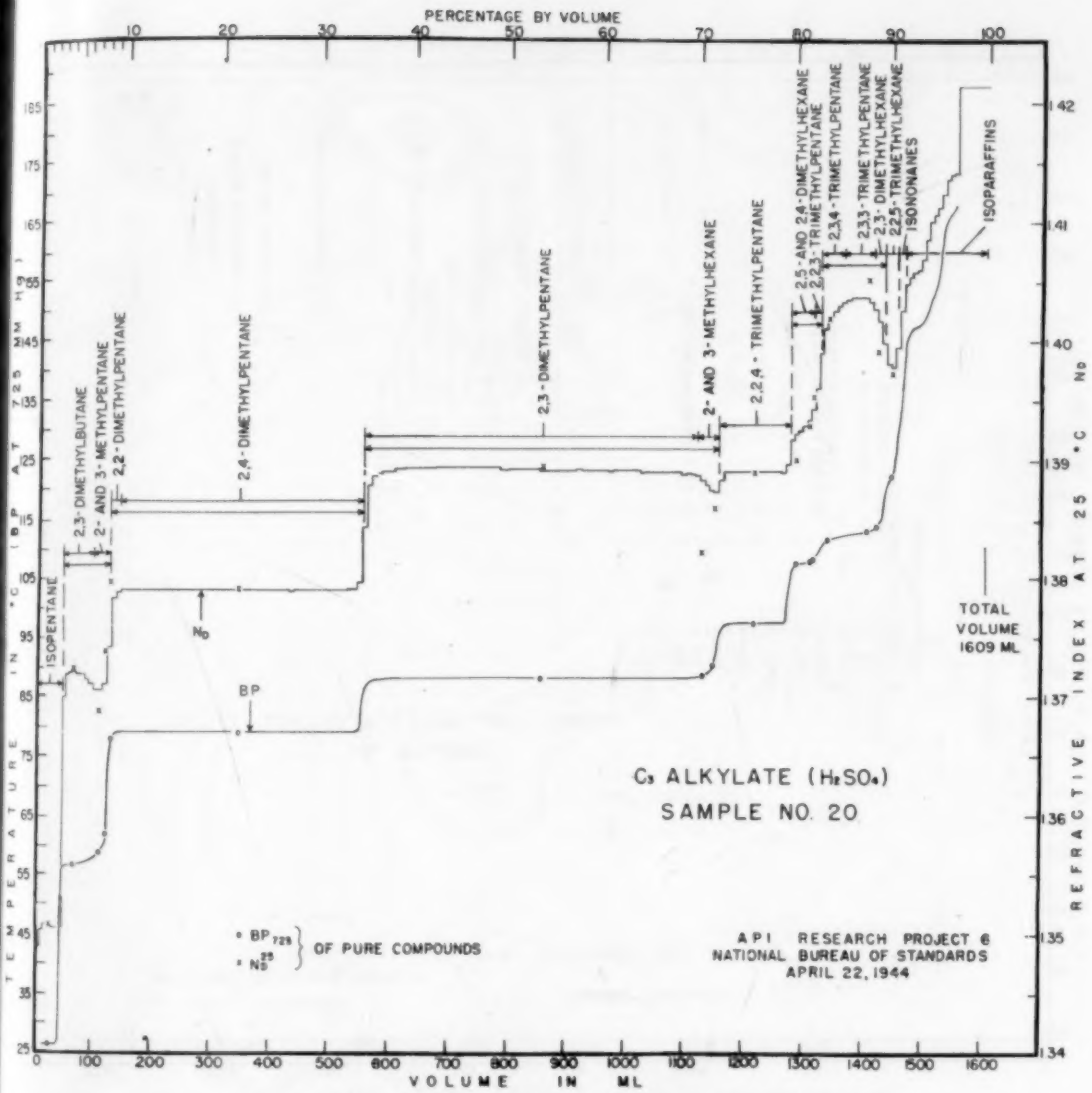

FIGURE 14.—*Results of the analytical distillation of* C_3 *alkylate* (H_2SO_4), *sample 20.*

Details are given in table 3.

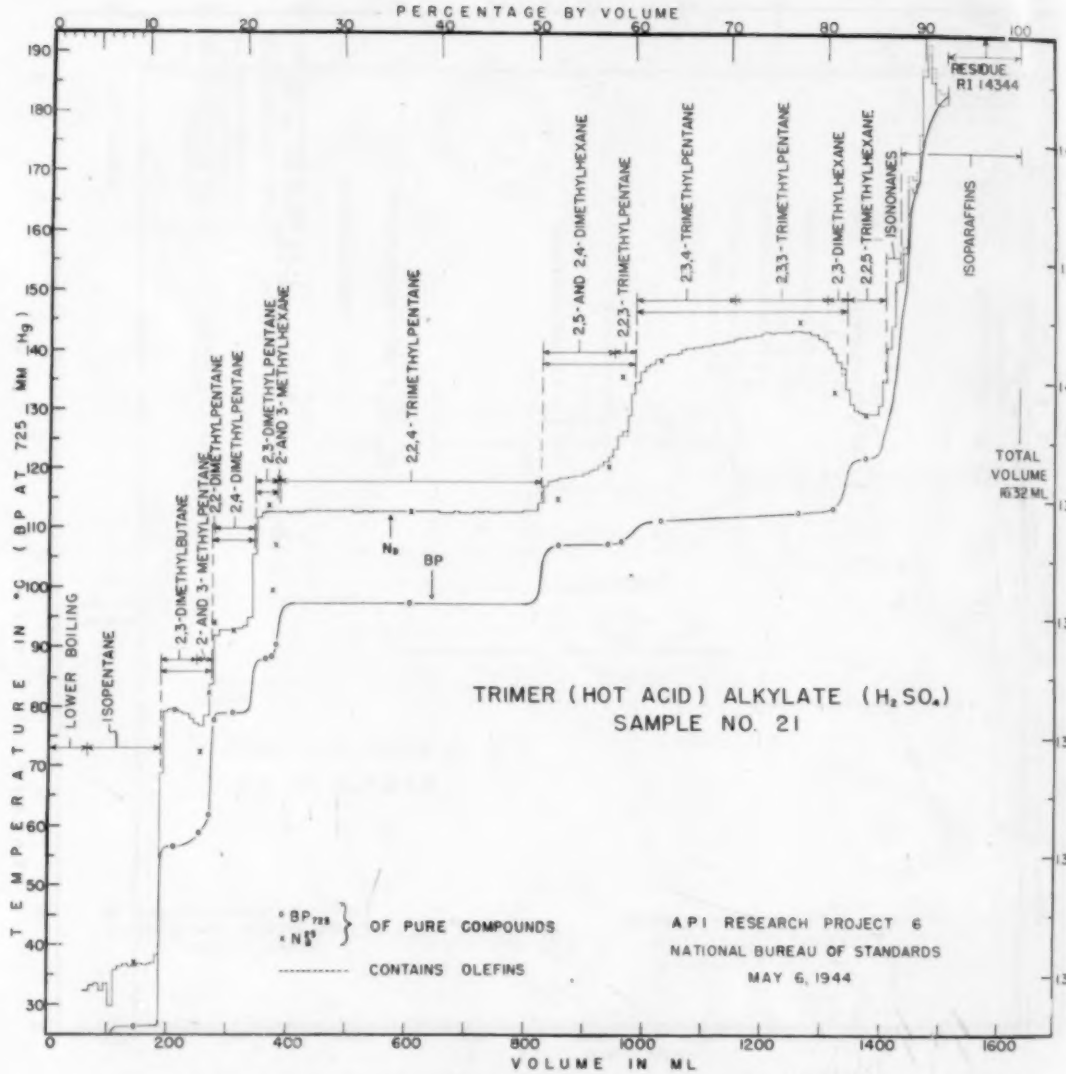

FIGURE 15.—*Results of the analytical distillation of trimer (hot-acid) alkylate (H_2SO_4), sample 21.*

Details are given in table 6.

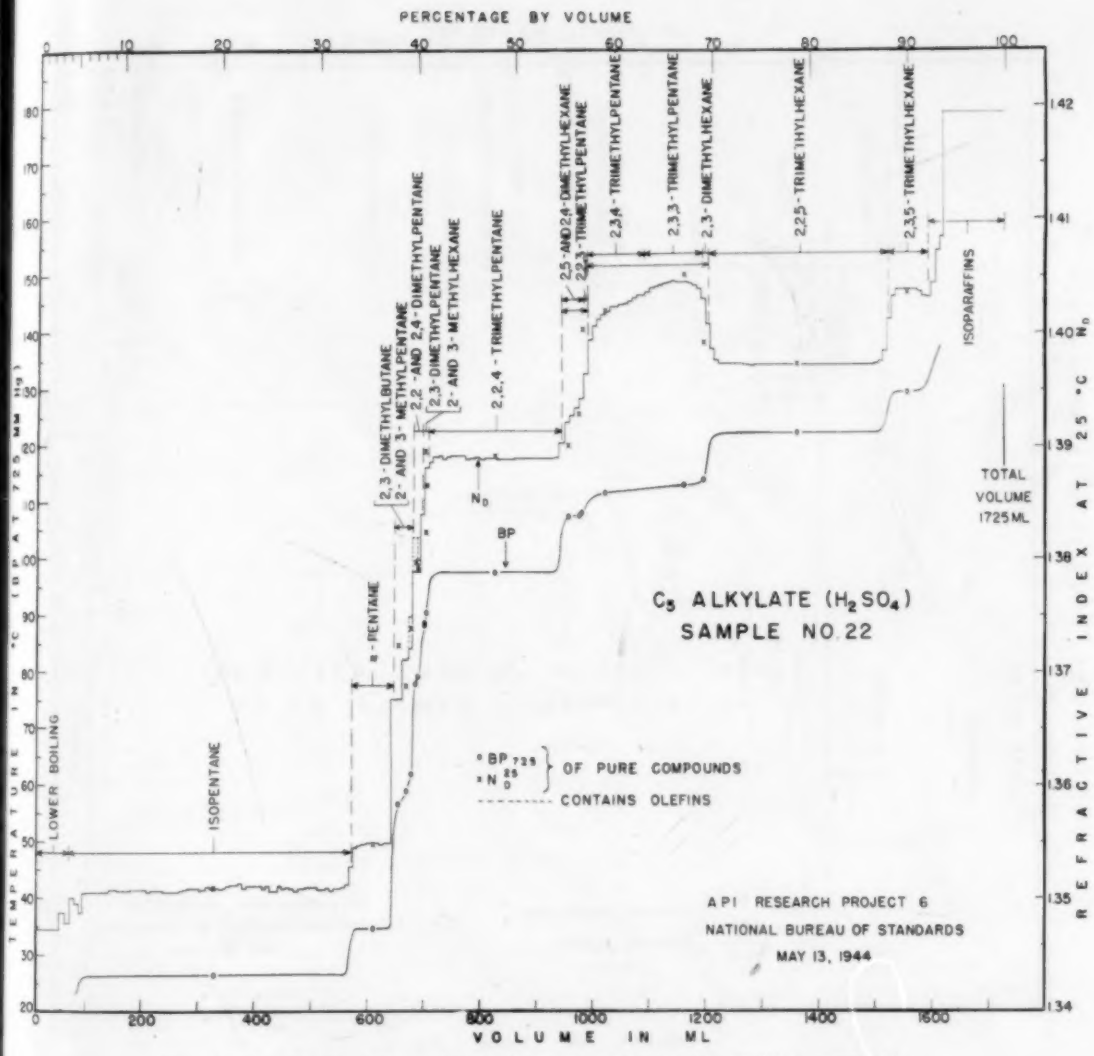

FIGURE 16.—*Results of the analytical distillation of* C_5 *alkylate* (H_2SO_4), *sample 22.*

Details are given in table 5.

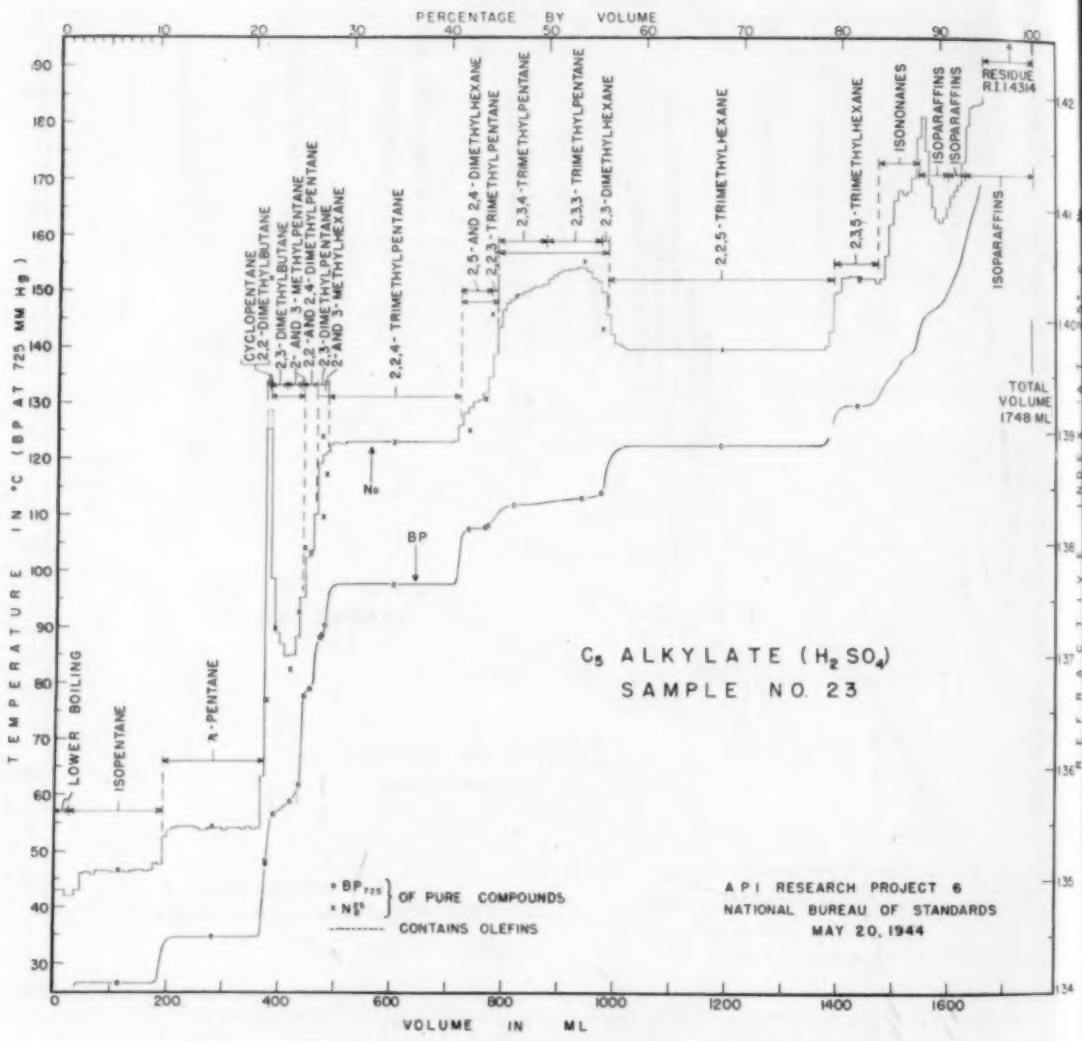

FIGURE 17.—*Results of the analytical distillation of* C_5 *alkylate* (H_2SO_4), *sample 23.*

Details are given in table 5.

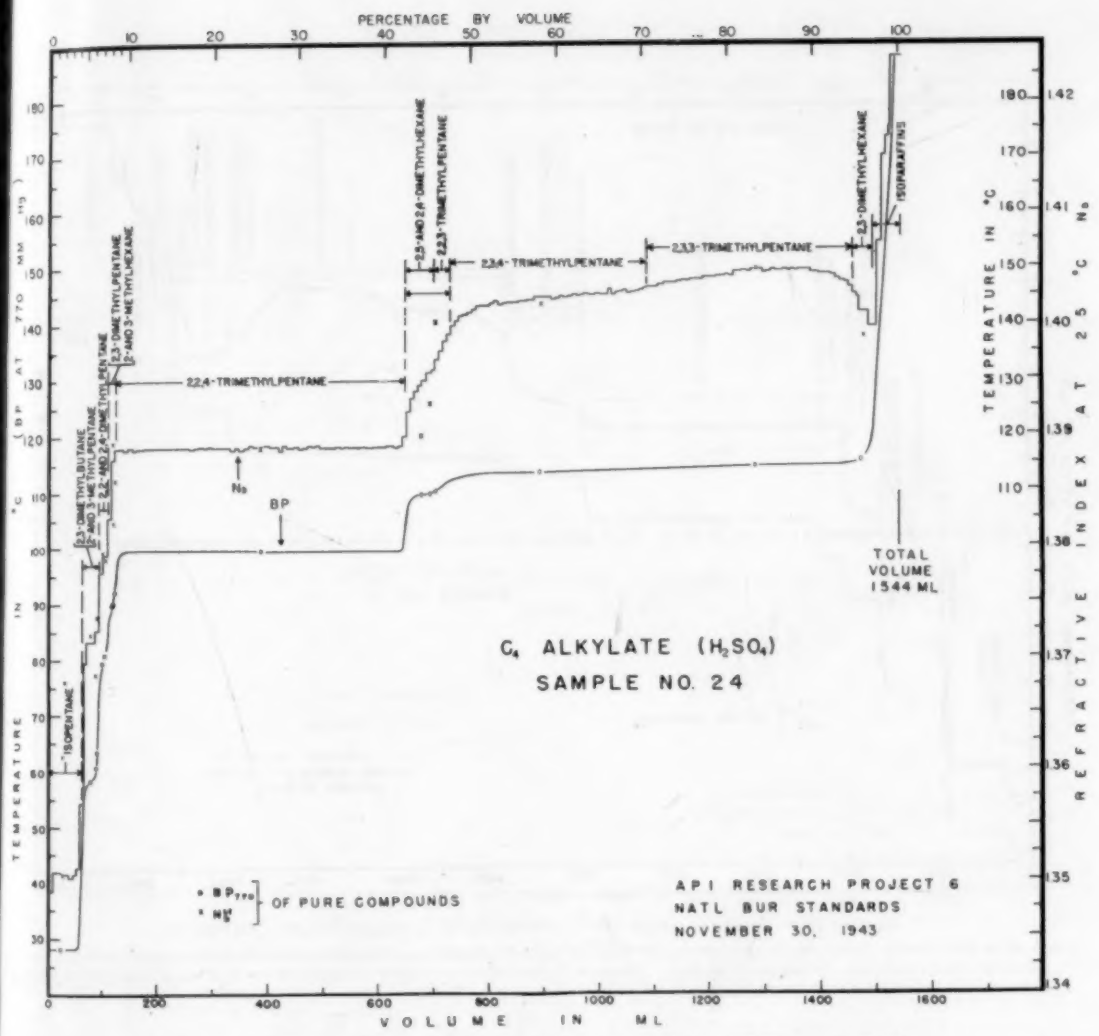

FIGURE 18.—*Results of the analytical distillation of* C_4 *alkylate* (H_2SO_4), *sample 24.*

Details are given in table 4.

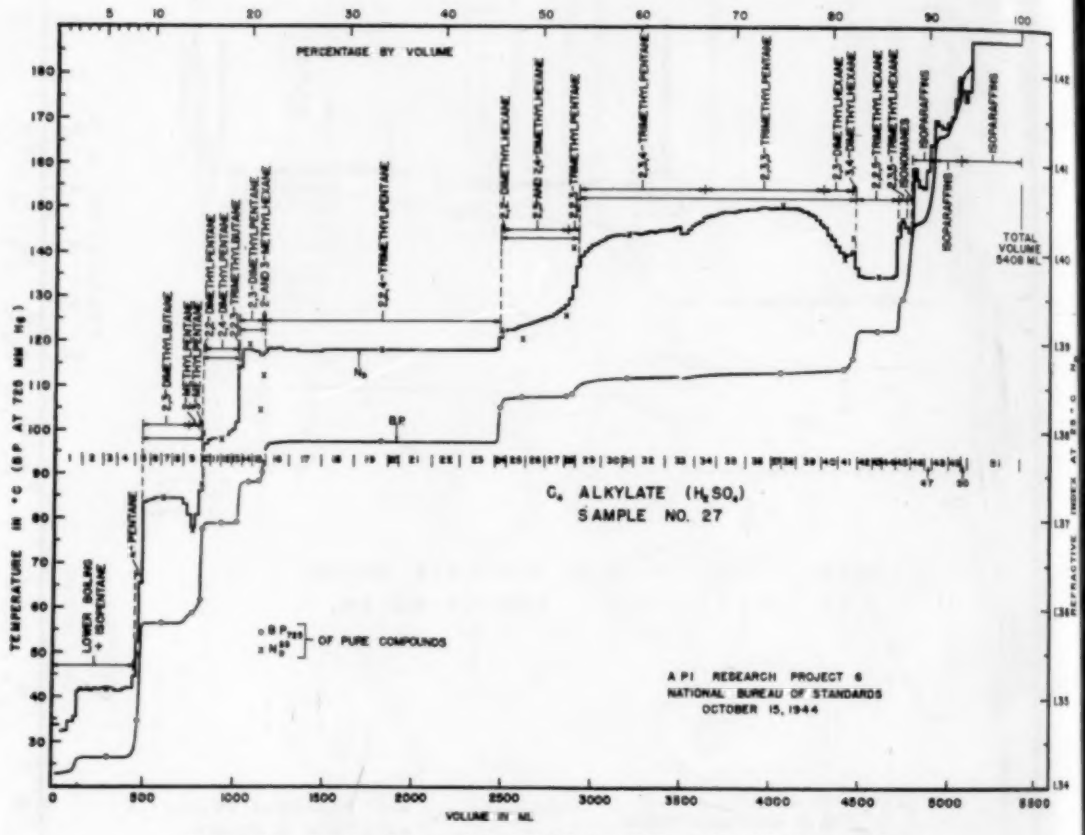

FIGURE 19.—*Results of the analytical distillation of* C_4 *alkylate* (H_2SO_4), *sample 27.*

Details are given in table 4. Near 3,500 ml, the lapse in the boiling-point curve was caused by a brief halting of the distillation, with the still being placed on total reflux before resumption of withdrawal of distillate. The dip in the refractive-index curve at this point reflects the effect of the additional reflux.

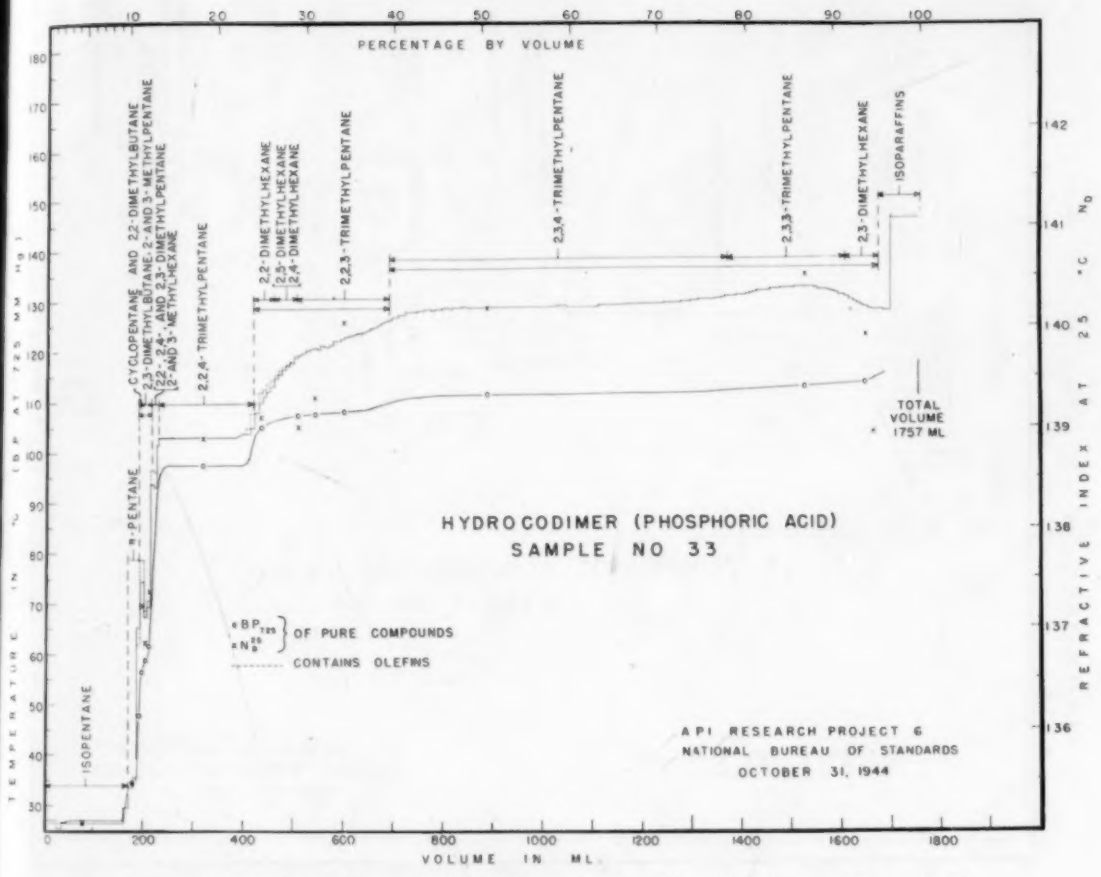

FIGURE 20.—*Results of the analytical distillation of hydrocodimer (phosphoric acid), sample 33.*

Details are given in table 7.

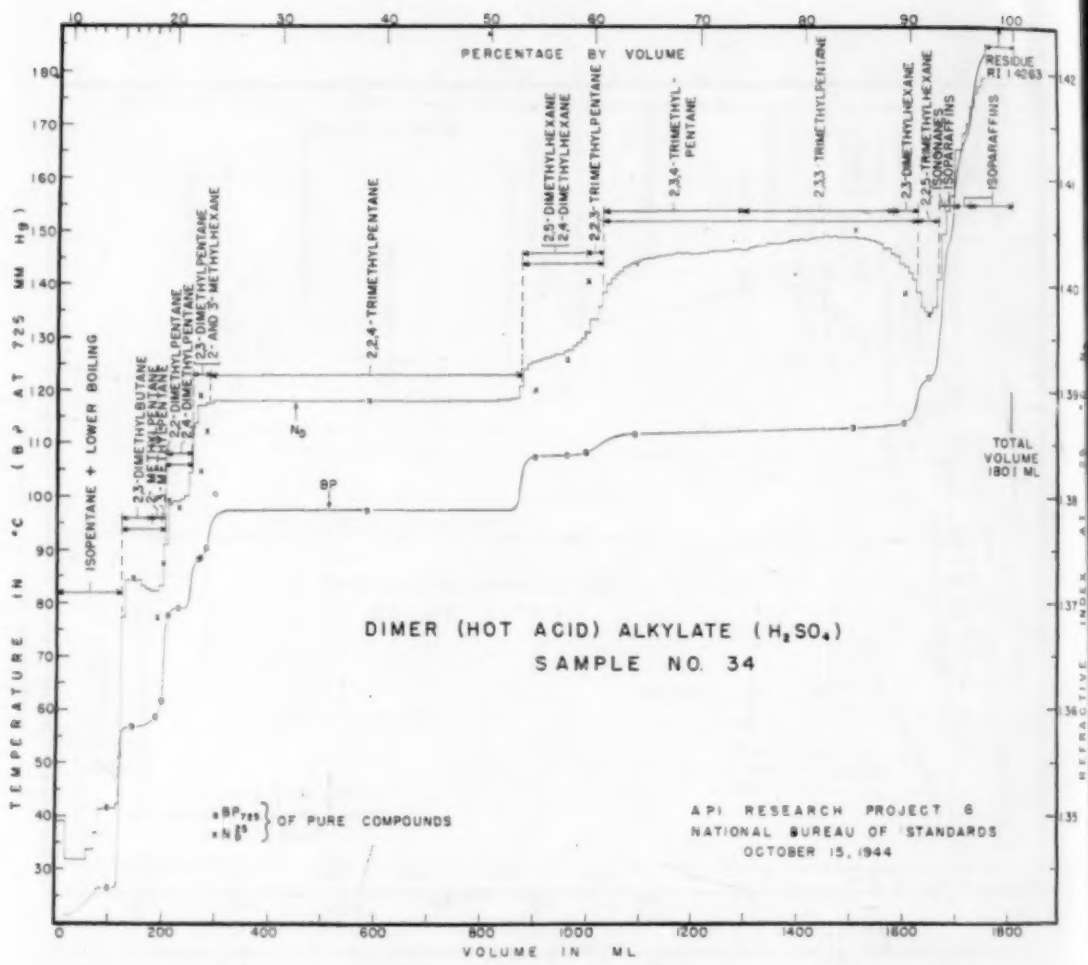

FIGURE 21.—*Results of the analytical distillation of dimer (hot-acid) alkylate* (H_2SO_4), *sample 34.*

Details are given in table 6.

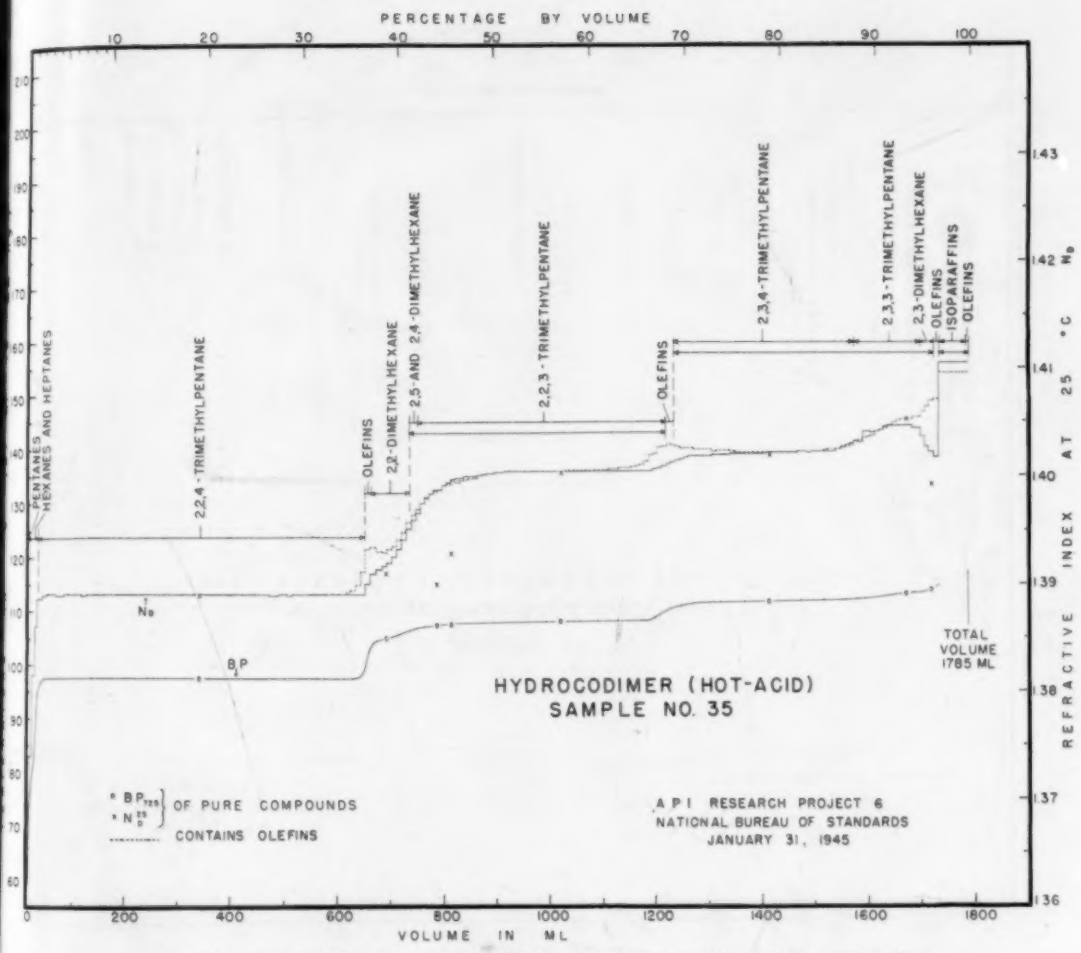

FIGURE 22.—*Results of the analytical distillation of hydrocodimer (hot-acid), sample 35.*

Details are given in table 7.

740279—47——9

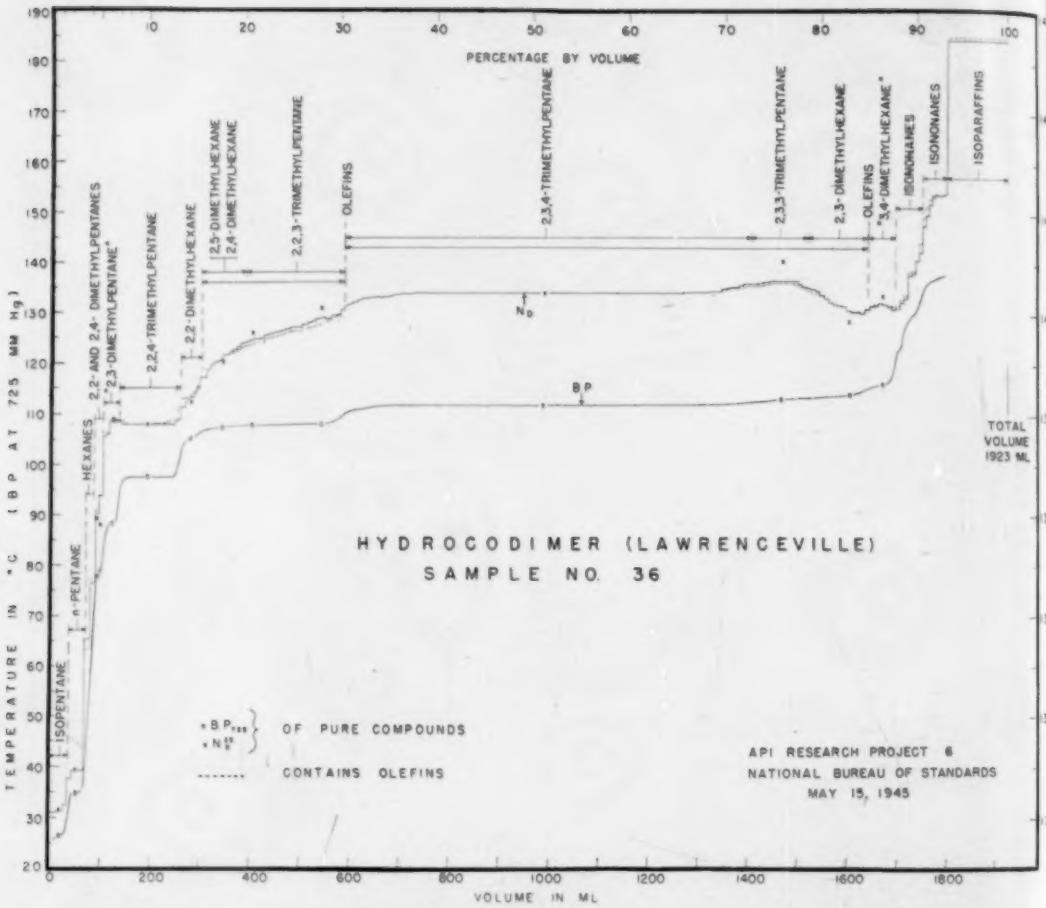

FIGURE 23.—*Results of the analytical distillation of hydrocodimer (Lawrenceville), sample 36.*

Details are given in table 7.

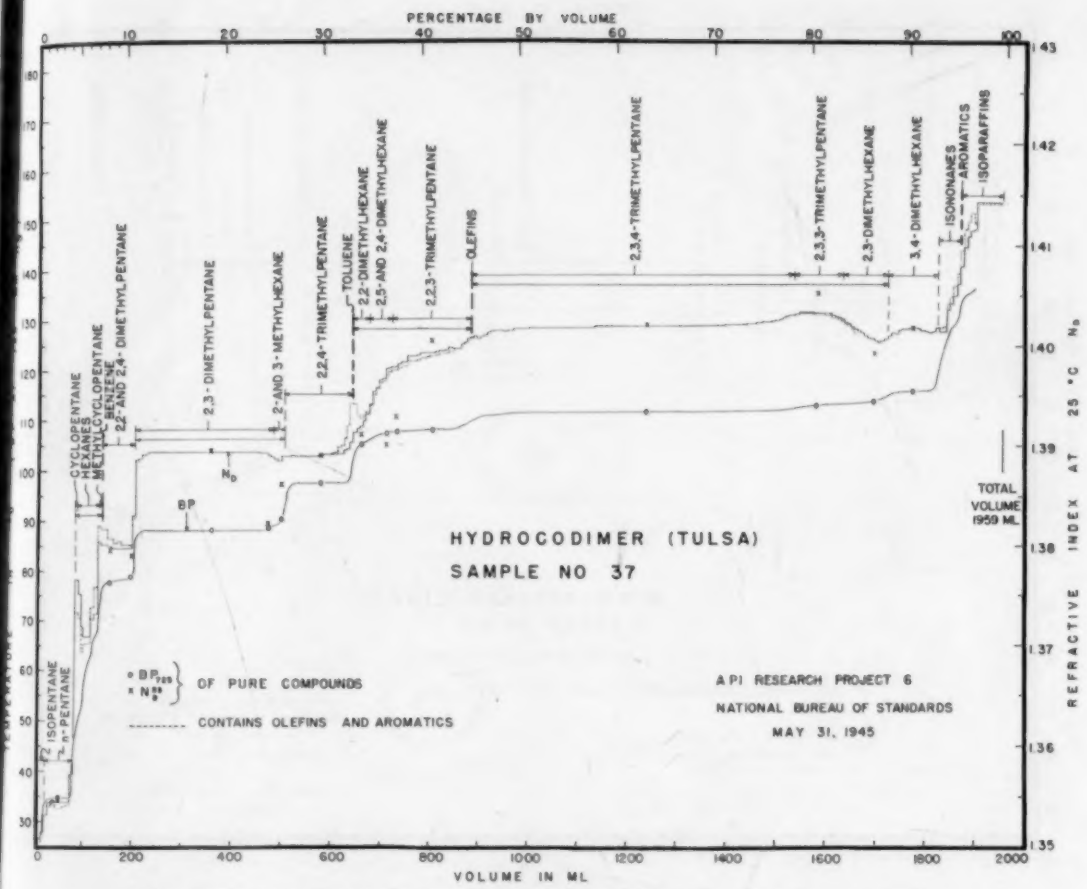

FIGURE 24.—*Results of the analytical distillation of hydrocodimer (Tulsa), sample 37.*

Details are given in table 7.

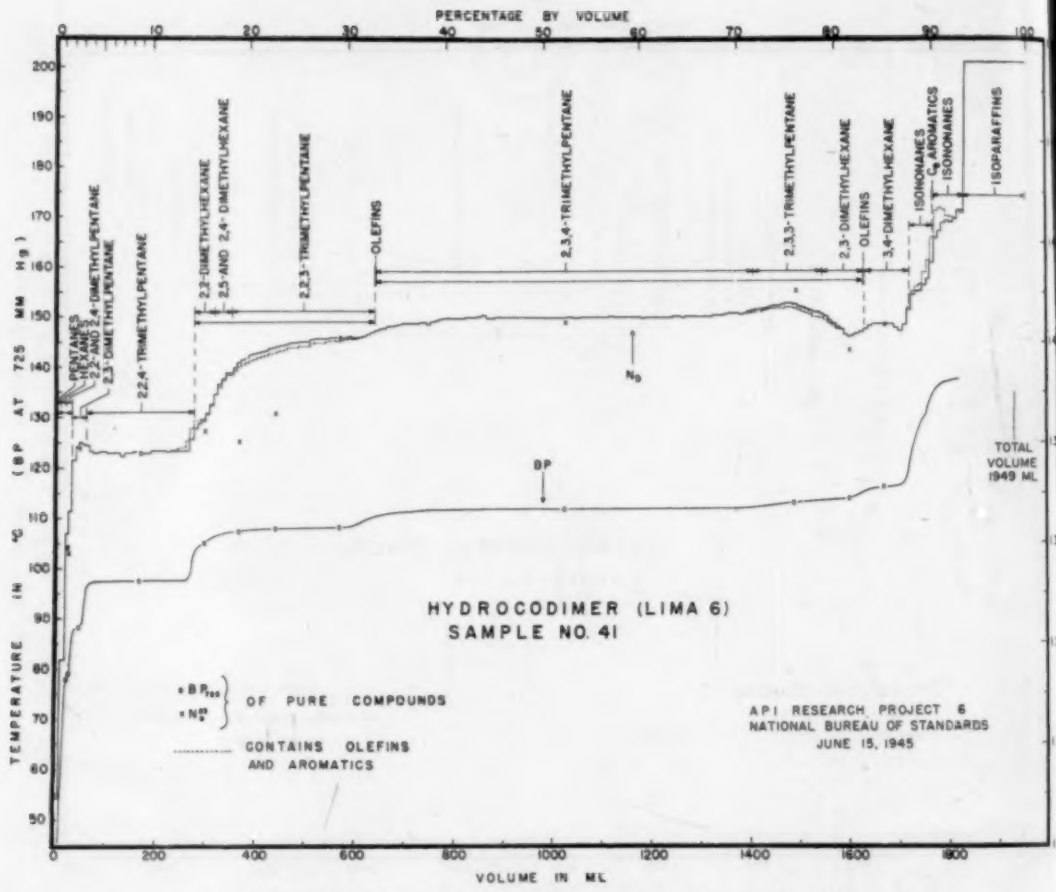

FIGURE 25.—*Results of the analytical distillation of hydrocodimer (Lima 6), sample 41.*

Details are given in table 7.

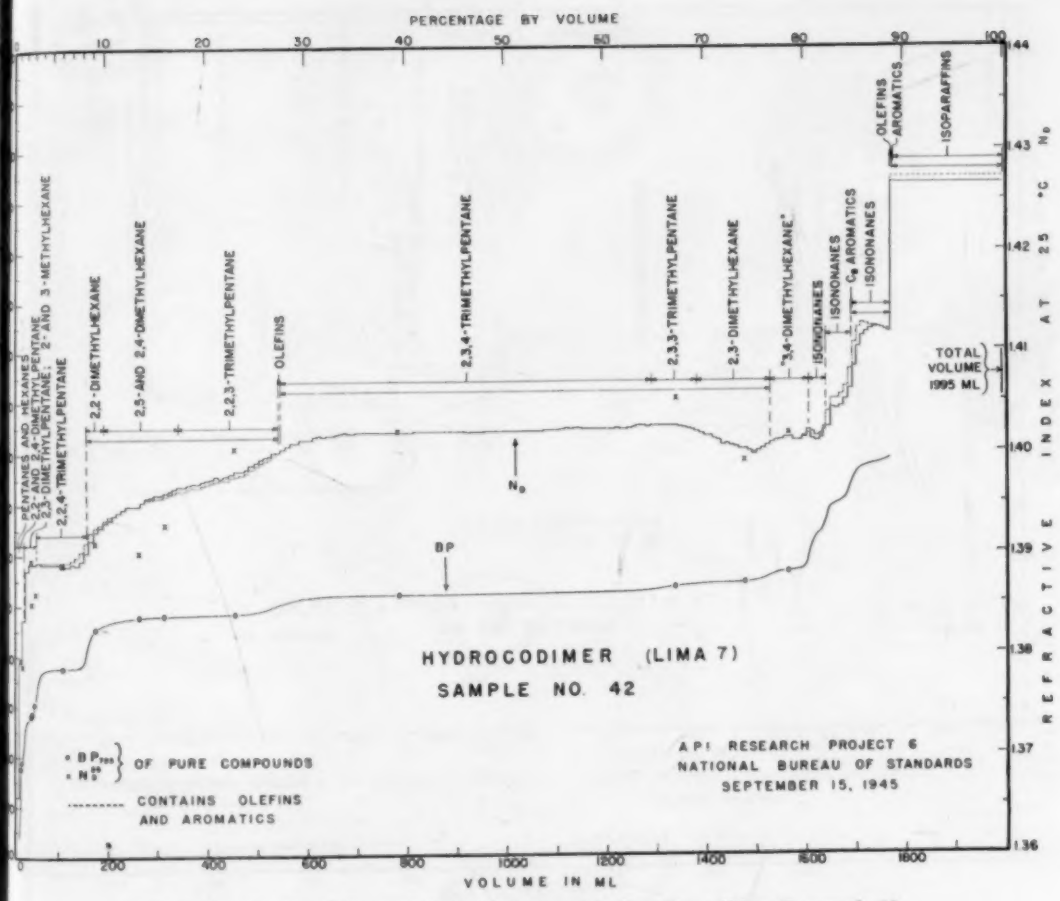

FIGURE 26.—*Results of the analytical distillation of hydrocodimer (Lima 7), sample 42.*

...s are given in table 7.

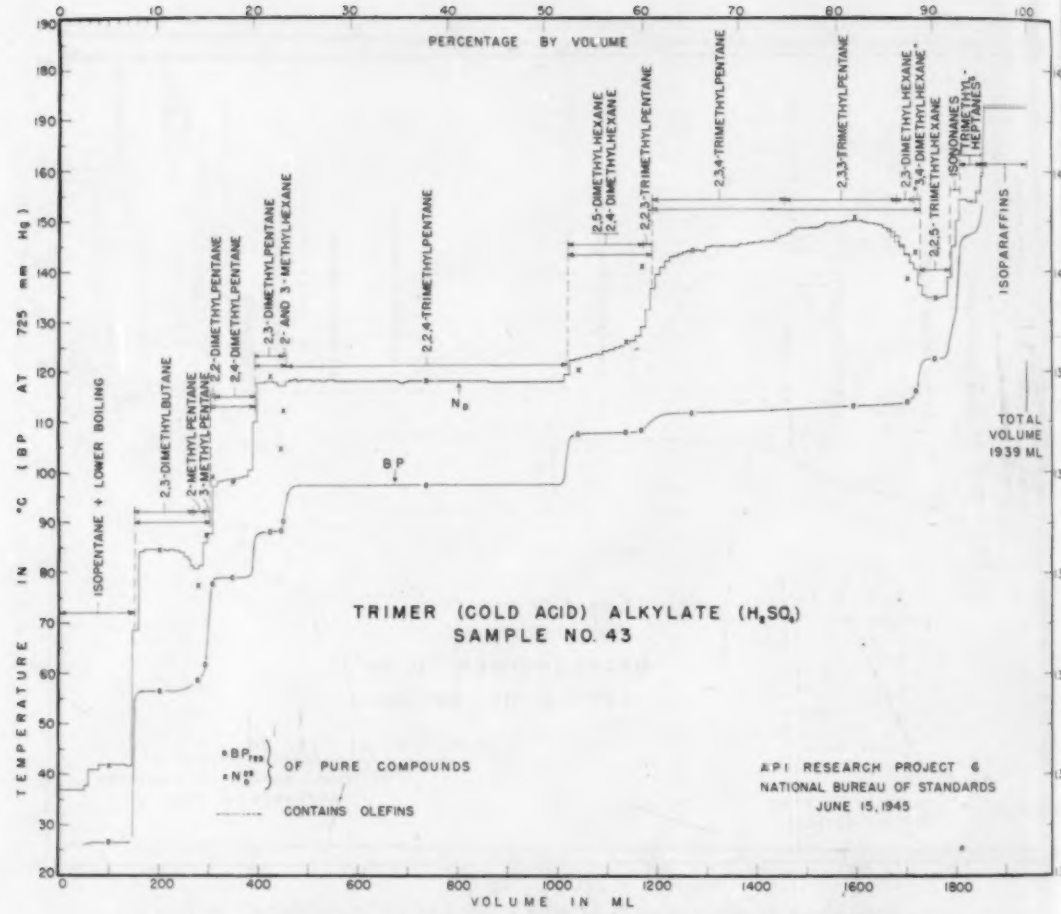

FIGURE 27.—*Results of the analytical distillation of trimer (cold-acid) alkylate* (H_2SO_4), *sample 43.*

Details are given in table 6.

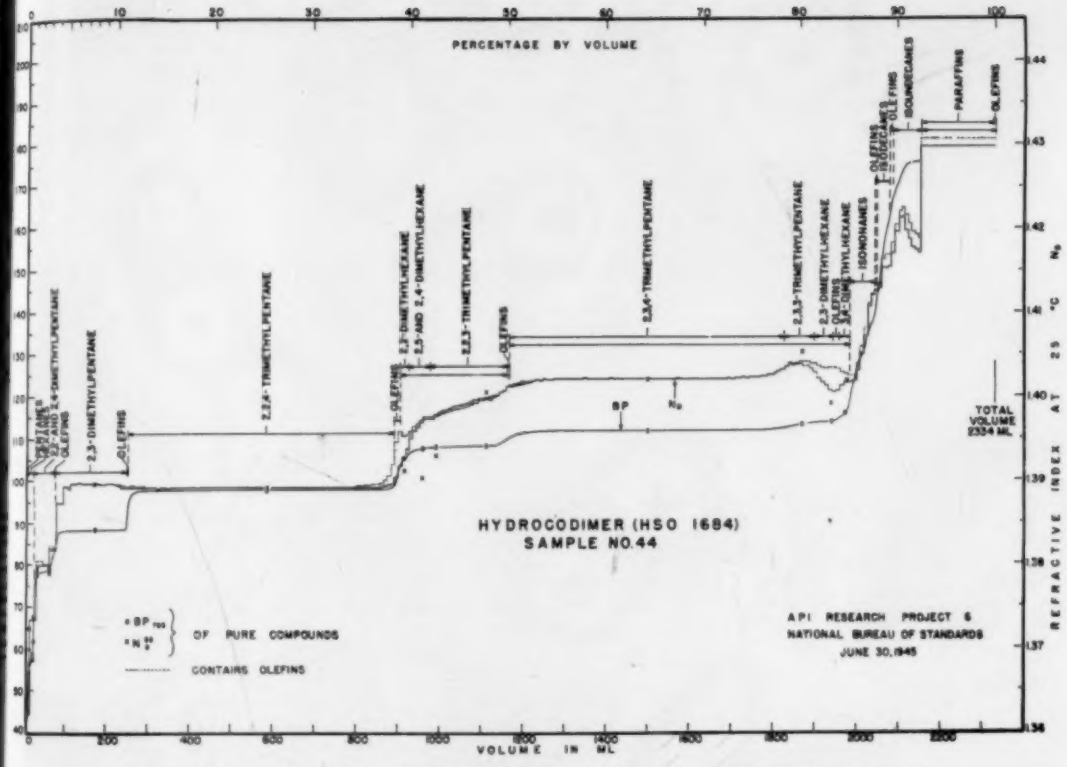

FIGURE 28.—*Results of the analytical distillation of hydrocodimer* (HSO–1684), *sample 44.*

tails are given in table 7.

ASHINGTON, September 16, 1946.